

Consequences of size dependence of transition probabilities in stochastic equations^{a)}

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We assume stochastic master equations for the temporal evolution of macroscopic systems with two or more accessible states. Such systems fall into two classes depending on the ratio of transition probabilities between microscopic states of a system, determined by detailed balance, which either scales, or does not, with the size of the system. The two classes have different properties in regard to (1) dependence of rate of transition between macroscopic states on the size of the system; (2) presence of separate time scales; and (3) sharpness of transition between macroscopic states. Thus we show that the stationary distribution function, through the condition of detailed balance, contains information about some properties of the temporal evolution.

I. INTRODUCTION

The theory of stochastic processes has been successfully applied to the study of the evolution of physical systems with many degrees of freedom.¹ Of special interest are systems that have two (or more) accessible states, for which the stochastic models provide a method for obtaining their evolution in time. Examples are chemical reactions, where the transition is from reactants to products; systems with equilibrium phase transitions; and far-from-equilibrium systems with multiple stationary states.

The behavior of such systems can be categorized into two classes. An example of the first class is the case of equilibrium phase transitions. When one of the phases is metastable with respect to the other, the evolution of the system is toward the equilibrium state with the complete disappearance of the metastable phase. We refer to this property as the "sharpness" of the transition from the metastable to the equilibrium state. The relaxation times of metastable states grow rapidly with the size of the system (the stochastic space). Furthermore, there is a wide separation of time scales in the evolution of the system. The characteristic time scale of fluctuations around a metastable or stable state is generally much shorter than the time of transition.

The second class includes phenomena like chemical reactions. When the reactants are energetically less stable than the products, the reaction proceeds until equilibrium is established between reactants and products. Thus the transition is not "sharp" in the sense discussed before. The relaxation times (rates of forward and reverse reaction) hardly change with the size of the stochastic space (the number of energy levels). There may not exist a distinct separation of time scales between energy redistribution in a molecule and the chemical reaction. The chemical reaction may affect considerably the distribution function for the molecular levels.

The aim of this paper is to address the issue of the basic properties of the stochastic equations of such systems which lead to the cited differences in behavior. It can be well argued that the differences between these two examples arise because one evolves on a free energy surface and the other on a potential energy surface. Although this is of course true, the question remains how that difference enters the master equations applicable to each class. Apart from the mathematical interest, there is also a practical reason for this question. There are some cases for which the choice of a stochastic model is not obvious. An example is the field of chemical instabilities.^{1b} The consequences of the analysis presented below may be of some help in choosing the stochastic models in such cases.

To carry out the analysis, we choose two typical examples from the two classes discussed above. One example is the mean field Ising model and the other is an isomerization reaction.

On the stochastic level of description, there is a deceptive similarity between these two examples. Consider a mean field Ising model with a small "down" magnetic field. The free energy per spin as a function of the number of "up" spins looks essentially as is shown in Fig. 1, upper panel.² A system that is prepared in the metastable state α will in a random walk escape over the barrier β until equilibrium is reached. Similarly, a simple isomerization reaction of the type $A \rightleftharpoons B$ can be represented as shown schematically in Fig. 1, lower panel. The molecule A is energetically less stable with respect to the molecule B. The isomerization can be described as a random walk on the energy levels and an escape over the barrier.³⁻⁵

There are, however, the differences of the two classes of systems. The relaxation time of the Ising-type metastable states grows rapidly with the number of spins (i. e., the number of steps in the random walk) present in the system.² Quite on the contrary, the relaxation times, or better, the rate constants of the chemical reaction, are weakly dependent on the number of levels (i. e., the number of steps in the random walk) and can be represented approximately in the Arrhenius form $k = A \exp(-Ea/RT)$, where Ea measures essentially the activation barrier. The characteristic behavior of

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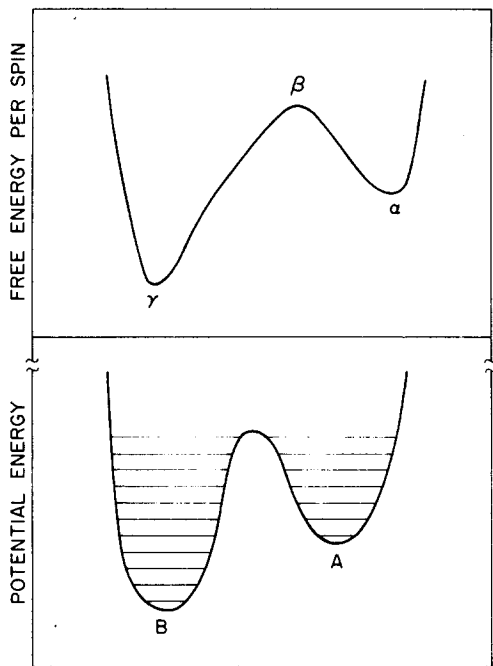


FIG. 1. Upper panel: The free energy per spin of an Ising system with a small down magnetic field, α and γ are the values of net magnetization that are locally stable. A system prepared in α will escape over the barrier until equilibrium is reached. Lower panel: A potential energy sketch for an isomerization reaction $A \rightleftharpoons B$. The reaction is described as a random walk along the levels. A reaction is an escape above the barrier. The differences in the macroscopic behavior due to the macroscopic constraints are attributed to different scaling properties of ratios of the transition probabilities.

phase transitions as already mentioned is that the realized state is the stable one, whereas the metastable state is evacuated completely from representative points during the relaxation.⁸ The chemical reaction attains equilibrium, and a finite ratio of concentrations is established, consistent with $[A]/[B] = \exp(\Delta G^0/RT)$.

We wish to establish in this article that the important quantity to consider in stochastic models is the ratio of probabilities for up and down transitions. Differences in the overall behavior of the two classes are due to differences in the scaling properties of these ratios with the size of the stochastic space. We argue that the differences discussed above are all determined by the presence or absence of these scaling properties.

Section II elaborates on the example of the mean field Ising model. The technique used is based on a method that was developed recently by Oppenheim, Shuler, and Weiss.⁶ We adopt the Hamiltonian and transition probabilities of Ref. 2 and show how the scaling properties mentioned above determine the dynamical and static behavior of the model.

In Sec. III we carry out a similar analysis for a chemical reaction. In Sec. IV we discuss the results, and connect the time dependent behavior with the stationary probability distribution. We show that from the same scaling properties that determine the temporal evolution it follows that the Ising model is characterized by an

effective unimodal distribution centered around the more stable state, whereas the chemical reaction shows a bimodal distribution. A general consequence is that every stochastic system whose stochastic model has scaled ratios of transition probabilities is characterized in the thermodynamic limit by a stationary effective unimodal distribution (except for the point of coexistence of the two accessible states).

II. TIME SCALES OF THE DYNAMICAL MEAN FIELD ISING MODEL

The mean field Ising model containing N spins in an external field H is described by the Hamiltonian²

$$H = - (J/N) \sum_{k < l} \sigma_k \sigma_l - B \sum_k \sigma_k - \frac{1}{2} J, \quad (1)$$

where B and J are constants. σ_k can have the value ± 1 . The problem can be discussed in terms of the single variable

$$j = \frac{1}{2} \left(N + \sum_i \sigma_i \right), \quad (2)$$

which is the number of up spins. Choosing $\mu = J = 1$, we have

$$H(j) = - \frac{(2j - N)^2}{2N} - B(2j - N). \quad (3)$$

At equilibrium, the probability distribution of finding j spins up depends on the temperature and is

$$P_e(j) = z^{-1} \binom{N}{j} \exp[-\beta H(j)], \quad (4)$$

where

$$z = \sum_j \binom{N}{j} \exp[-\beta H(j)]. \quad (5)$$

Defining the free energy per spin by

$$a(j, T) = \frac{kT}{N} \ln \binom{N}{j} + \frac{H(j)}{N}, \quad (6)$$

we can cast (4) into the useful form

$$P_e(j) = z^{-1} \exp[-N\beta a(j, T)]. \quad (7)$$

It is well known² that $a(j, T)$ has a different functional form at high and low temperatures. Above the Curie temperature T_c , it has one minimum, whereas at temperatures that are lower than T_c , it has two minima as a function of j . In the absence of a magnetic field these two minima have the same depth, whereas an application of a small magnetic field creates a metastable and stable state as sketched in Fig. 1.

The temporal behavior of the model is described by a stochastic equation of the birth and death type. An underlying assumption is that the system interacts with a heat bath and the master equation is

$$\frac{dP(j)}{dt} = \sum_{j'=j-1}^{j+1} P(j') L_{j',j}. \quad (8)$$

We choose the same transition probabilities as in Ref. 2:

$$L_{j,j+1} = \alpha \frac{N-j}{N} \exp\{-\frac{1}{2}\beta[H(j+1) - H(j)]\}, \quad (9)$$

$$L_{j,j-1} = \alpha \frac{j}{N} \exp\{-\frac{1}{2}\beta[H(j-1) - H(j)]\}$$

$$L_{jj} = -L_{j,j+1} - L_{j,j-1}.$$

It is important to stress at this point that the exact form of the transition probabilities is not essential for our analysis. The scaling properties are the important features of the transition probabilities and the choice of this model is just an example of a *type* of transition probabilities. The discussion of the temporal behavior will be based on the concept of mean first passage time.^{6,7} While introducing the quantities needed for the analysis, we shall prove two properties of the stationary, equilibrated system for $T < T_c$:

(i) The equilibrium distribution $P_e(j)$ has three extrema, located at those j for which $a(j+1, T) = a(j, T)$. We denote these points by $\gamma < \beta < \alpha$ and argue that P_e has maxima at γ and α and a minimum at β .

(ii) The maxima of $P_e(j)$ at α and γ become extremely sharp as $N \rightarrow \infty$. At a later point of the discussion we shall further prove that $P_e(\alpha)/P_e(\gamma)$ is either 0 or infinity in the thermodynamic limit, depending on which state is more stable.

The dynamical property that we wish to prove is

(iii) The ratio of the mean times for a system initially at $j = j_0$, $\beta < j_0 < \alpha$, to reach β to the mean time to reach α goes to infinity in the thermodynamic limit.

We start with the equilibrium distribution of the stochastic model and write it in the form⁸

$$P_e(j) = \frac{\theta_j}{1 + \sum_{j=1}^N \theta_j}; \quad (10)$$

the quantity θ_j is defined by

$$\theta_j = G_0 G_1 \cdots G_{j-1}, \quad (11)$$

where

$$G_j = \frac{L_{j,j+1}}{L_{j+1,j}} = \frac{N-j}{j+1} \exp\{-\beta[H(j+1) - H(j)]\}. \quad (12)$$

At this stage we introduce the scaling: consider the scaled variable

$$x = \frac{2j - N}{N}. \quad (13)$$

Clearly, $-1 < x < 1$, and

$$H(j+1) - H(j) = -2\left(x + \frac{1}{N}\right) - 2B; \quad (14)$$

thus, to order $1/N$,

$$G(x) = \frac{1-x}{1+x} \exp[2\beta(x+B)]. \quad (15)$$

As x is a scaled variable, $G(x)$ is independent of N . We locate the extrema in $P_e(j)$ from the condition $P(j_{ex})$

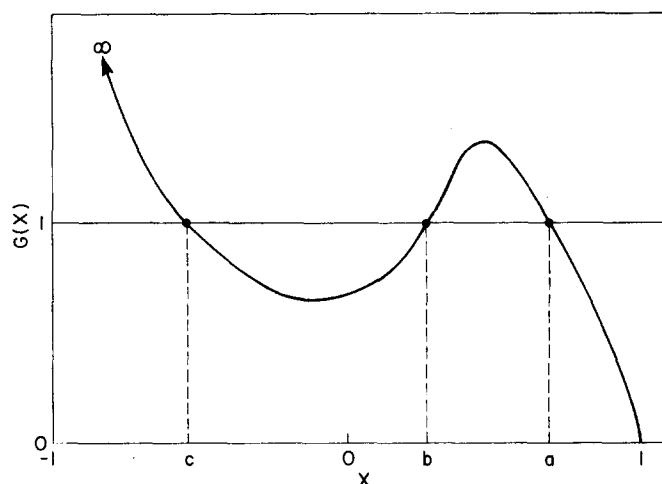


FIG. 2. The functional dependence of G on the scaled variable x . $G(x)$ is of order unity except for the neighborhood of $x = -1$. The parameters a , b , and c are related to α , β , γ according to $a = (2\alpha - N)/N$, etc. The points for which $G(x) = 1$ are the extrema of the stationary probability distributions. Negative slope is consistent with a maximum, and a positive slope with a minimum.

$= P(j_{ex} + 1)$ which is transformed to $G(x) = 1$. This condition is realized if the equation

$$\exp(-2\beta x) = \exp(2\beta B)(1-x)/(1+x) \quad (16)$$

is satisfied. It is easy to verify that when $\beta > 1$, Eq. (16) has three solutions, denoted in the sequel as $x = c, b, a$.

As $G(x)$ is infinite for $x = -1$ and vanishes for $x = 1$, the sketch in Fig. 2 represents the functional dependence of $G(x)$. From (10) and (11) it is clear that when $G(x)$ passes unity with a negative slope the stationary distribution has a maximum, and when the slope is positive P_e has a minimum. From this and the definition of G we see that our first point (i) is proved.

The consequences of the scaling will be apparent now, when we prove the second point, namely, the sharpness of the peaks of $P_e(j)$. Consider a number $\sigma \neq \alpha$, such that $\beta < \sigma < N$. The ratio of $P_e(\alpha)$ and $P_e(\sigma)$ is

$$R = \frac{P_e(\alpha)}{P_e(\sigma)} = \frac{\theta_\alpha}{\theta_\sigma} = \begin{cases} \prod_{j=\sigma}^{\alpha} G_j & \sigma < \alpha \\ \left(\prod_{j=\alpha}^{\sigma} G_j\right)^{-1} & \sigma > \alpha, \end{cases} \quad (17)$$

where we used the fact that $G(\alpha) = 1$. For $\sigma < \alpha$ we get

$$\ln R = \sum_{j=\sigma}^{\alpha} \ln G_j = N \sum_{j=\sigma}^{\alpha} \frac{1}{N} \ln G(j). \quad (18)$$

Using now the scaled variable and the scaling property we pass to integration,

$$\ln R = \frac{N}{2} \int_{(2\sigma-N)/N}^{\alpha} \ln G(x) dx. \quad (19)$$

$G(x)$ equals unity at a and b and for $\sigma < \alpha$ it is greater than unity all over the range of integration (Fig. 2). Thus, $R = e^{N\theta(1)}$. Similarly, if $\sigma > \alpha$,

$$\ln R = -\frac{N}{2} \int_{\alpha}^{(2\sigma-N)/N} \ln G(x) dx, \quad (20)$$

but now $G(x)$ is always smaller than unity (Fig. 2) and the integral is negative. Thus, for all $\beta < \sigma < N$

$$R = \exp[N\theta(1)], \quad (21)$$

where $\theta(1)$ is a positive quantity. Thus in the thermodynamic limit the equilibrium distribution is sharply peaked around α . A similar argument holds, of course, for γ .

We stress that this result will hold for any stochastic model provided that the ratio of transition probabilities has the scaling properties used here.

To prove our third point concerning the dynamical behavior of the model we consider two mean first passage times (m.f.p.t.). A system that is prepared at some $\beta < j_0 < \alpha$ can slide down the well towards α or climb up to escape over the barrier β . First we calculate the m.f.p.t. to get into α , denoted $T_{\alpha}(j_0)$. The expressions for the m.f.p.t. are derived in the Appendix in some detail, using the method developed recently by Oppenheim, Shuler, and Weiss.⁶ When α is an absorbing barrier and β a reflecting one, we have from Eq. (A17)

$$T_{\alpha}(j_0) = \sum_{j=\beta}^{j_0} \psi_j + \sum_{j=r+1}^{\alpha} \chi_j, \quad (22)$$

where

$$\psi_j = \frac{1}{L_{\alpha, \alpha+1}} \frac{\theta_j}{\theta_{\alpha}} + \frac{1}{L_{\alpha-1, \alpha}} \frac{\theta_j}{\theta_{\alpha-1}} + \dots + \frac{1}{L_{j_0, j_0+1}} \frac{\theta_j}{\theta_{j_0}}, \quad (23)$$

$$\chi_j = \frac{1}{L_{\alpha, \alpha+1}} \frac{\theta_j}{\theta_{\alpha}} + \frac{1}{L_{\alpha-1, \alpha}} \frac{\theta_j}{\theta_{\alpha-1}} + \dots + \frac{1}{L_{j, j+1}} \frac{\theta_j}{\theta_j}, \quad (24)$$

and θ_j is as defined in (11). We can bound the m.f.p.t. from above relatively easily.⁶ First we remember that in the interval $\beta < j < \alpha$ the factor $L_{j, j+1}$ is always positive. Denote its lower bound by \hat{L} . Consider now the expressions for ψ_j, χ_j . The index of θ in the numerator is always smaller than the index in the denominator. As G_j is greater than unity in this range, every factor θ_p/θ_q that appears in ψ_j or χ_j is smaller or equal to 1. Thus we may replace them all by 1 and simply count the number of terms. The upper bound is then

$$T_{\alpha}(j_0) < \frac{1}{\hat{L}} \left((N-r+1)(j_0-\beta+1) + \frac{(N-r+1)(N-r)}{2} \right), \quad (25)$$

and as \hat{L} is $\theta(1)$, we have

$$T_{\alpha}(j_0) < \theta(N^2). \quad (25')$$

This conclusion changes dramatically when we consider the other passage time, namely, for the escape over the barrier. Now β is an absorbing barrier and α is a reflecting one and [Appendix, Eq. (A29)]

$$T_{\beta}(j_0) = \sum_{j=\beta}^{j_0-1} \tilde{\chi}_j + \sum_{j=j_0}^{\alpha} \tilde{\psi}_j, \quad (26)$$

with

$$\tilde{\chi}_j = \frac{1}{L_{\beta+1, \beta}} \frac{\tilde{\theta}_j}{\tilde{\theta}_{\beta+1}} + \frac{1}{L_{\beta+2, \beta+1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_{\beta+2}} + \dots + \frac{1}{L_{j, j-1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_j}, \quad (27)$$

$$\tilde{\psi}_j = \frac{1}{L_{\beta+1, \beta}} \frac{\tilde{\theta}_j}{\tilde{\theta}_{\beta+1}} + \frac{1}{L_{\beta+2, \beta+1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_{\beta+2}} + \dots + \frac{1}{L_{j_0, j_0-1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_{j_0}}, \quad (28)$$

where

$$\tilde{\theta}_j = \frac{1}{G_{\alpha-1}, G_{\alpha-2}, \dots, G_j}. \quad (29)$$

In the range $\beta < j_0 < \alpha$, $L_{j, j+1}$ is bounded and we denote its upper bound by \bar{L} . Each term in $\tilde{\chi}_j$ and of $\tilde{\psi}_j$ now involves a ratio of θ_j 's such that the upper index is lower than the lower one. Since all the G_j are greater than unity in this range, we can obtain a lower bound for $T_{\beta}(j_0)$ by picking the largest term in each sum. Clearly

$$T_{\beta}(j_0) > \frac{1}{\bar{L}} [G_{\beta} \dots G_{\alpha} + G_{j_0} \dots G_{\alpha}]. \quad (30)$$

We invoke again now the scaling property. The first term in the brackets is R_1 and the second R_2 , where

$$\ln R_1 = \sum_{j=\beta}^{\alpha} \ln G_j; \quad \ln R_2 = \sum_{j_0}^{\alpha} \ln G_j, \quad (31)$$

and as before,

$$\ln R_1 = N \int_{\beta}^{\alpha} \ln G(x) dx; \quad \ln R_2 = N \int_{(2j_0-N)/N}^{\alpha} \ln G(x) dx, \quad (32)$$

and

$$T_{\beta}(j_0) > \frac{1}{\bar{L}} \exp[N\theta(1)]. \quad (33)$$

The final conclusion is that

$$\lim_{N \rightarrow \infty} \frac{T_{\beta}(j_0)}{T_{\alpha}(j_0)} = \infty, \quad (34)$$

and our third point is proved. We reiterate that (34) is not special to the model considered here and will hold for any system whose dynamical properties and thermodynamic constraints impose scaled ratios of transition probabilities.⁶ To see that models without the scaling property behave differently, we turn now to the chemical transformation.

III. TIME SCALES FOR A CHEMICAL REACTION MODEL

We can simplify the discussion on the chemical transformation by adopting the simplistic Montroll-Shuler⁵ treatment of unimolecular decomposition. The central assumption in this model is that the random walk can be described as if the molecules are perfect harmonic oscillators, and the transition probabilities are determined by the quantum mechanical treatment of Landau and Teller:

$$L_{ij} = 0 \quad \text{for } |i-j| > 1, \\ L_{j, j+1} = -\kappa(j+1)e^{-\theta}, \quad L_{j, j-1} = -\kappa j, \quad (35)$$

where κ is a rate parameter and θ is the vibrational spacing divided by kT . Although this model is somewhat oversimplified and unrealistic, the essential difference between the chemical transformation and the previous example is fully contained in it. We adopt this model by considering the $N+1$ st level of one molecule (say, A) connected to the $M+1$ st level of the other molecule (B). Each of these levels is considered as an absorbing barrier when the mean first passage time is calculated for the transformation $A \rightarrow B$ and $B \rightarrow A$, respectively. These passage times are identical with the so-called "flux coefficients" of the chemical reactions, and a full evaluation and critique of their use can be found in a review article by Widom.⁴

Consider now the following question: suppose that we fix the activation barrier, namely, the energy difference between the levels 0 and $N+1$ and $M+1$, respectively. Now increase the number of levels (the analogue of the number of spins in the previous example). The first thing to notice is that the ratio $L_{j,j+1}/L_{j+1,j}$ behaves very different now when N is increased. In the previous example the scaling property guaranteed that $G(x)$ is independent of N . Here this ratio is dependent on N and approaches unity as $N \rightarrow \infty$. To bring the difference in the scaling properties into full view, we consider again the mean first passage time. If the N th level is now an absorbing barrier, and the zeroth level is a reflecting one, then for molecule A [see (A14)]

$$T = \frac{\eta_{N+1}}{\theta_{N-1}} \sum_{j=0}^N \theta_j - \sum_{j=0}^N \eta_j. \quad (36)$$

It was shown previously⁵ that for this case $\theta_j = e^{-j\theta}$,

$$\eta_j = \frac{1}{\kappa} \left(\frac{1}{j} + \frac{e^{-\theta}}{j-1} + \frac{e^{-2\theta}}{j-2} + \cdots + \frac{e^{-(j-1)\theta}}{1} \right), \quad (37)$$

and T is solved analytically,

$$T = \frac{1}{\kappa(1-e^{-\theta})} \sum_{j=1}^{N+1} \frac{e^{j\theta-1}}{j}. \quad (38)$$

Multiplying and dividing by N we get

$$T = \frac{1}{\kappa(1-e^{-\theta})} \sum_{j=1}^{N+1} \left(\frac{\exp(j\Delta E/kTN)}{N(j/N)} - \frac{1}{N(j/N)} \right). \quad (39)$$

This quantity can be easily bounded from above by

$$T < \frac{1}{\kappa(1-e^{-\theta})} \sum_{j=1}^{N+1} \frac{1}{N} \exp\left(\frac{j\Delta E}{kTN}\right), \quad (40)$$

and when we let N grow,

$$T < \frac{1}{\kappa(1-e^{-\theta})} \int_{1/N}^1 \exp\left(\frac{\Delta E x}{kT}\right), \quad (41)$$

with $x = j/N$. Thus

$$T < \frac{kT}{\kappa\Delta E(1-e^{-\theta})} \left[\exp\left(\frac{\Delta E}{kT}\right) - \exp(-\theta) \right]. \quad (42)$$

We see that even with this crude bound we do not get anything like the exponential growth of the passage time, Eq. (33), with the number of the steps in the random walk. Better calculations of the passage time leave this observation unaltered: The passage time in this case depends essentially only on the activation barrier and not on the number of the levels, in agreement with the

Arrhenius form for the reaction rates.

IV. DISCUSSION

We have considered two classes of systems which have two or more states. The prototype of one of them is an ordinary chemical reaction of the type $A \rightleftharpoons B$. The potential energy surface of this example has two wells corresponding to the locally stable species A and B. The temporal evolution of the system is calculated with a stochastic master equation for the random walk in the molecular phase space. The chemical reaction occurs when representative points escape over the potential barrier. In equilibrium, the two species coexist with a fixed proportion between them.

The prototype of the other class is the mean field Ising model. At temperatures below the Curie temperature, the system has two locally stable states corresponding to the two directions of the net magnetization. A small external magnetic field causes one of the states to become metastable. The relaxation of an initial state is described by means of a master equation in the number of up spins as a stochastic variable. The transition is again occurring when representative points escape over the barrier. The interesting characteristics of these two prototypes, however, are manifested by the differences between them. We concentrate now on the differences, and argue that they demand different scaling properties of the ratios of transition probabilities.

(i) Both prototypes may in principle have two different time scales in their dynamical behavior. The shorter one is the relaxation to the local quasistationary state, and the longer is the diffusion across the barrier. The difference between the two classes is that the separation between these time scales grows with the size of the system in the Ising-type case, and is unaffected essentially when the number of levels grows in the chemical example. We showed in Secs. II and III that this is a consequence of the different scaling of the ratios of transition probabilities.

(ii) The equilibrium distribution is in principle bimodal in both cases. The Ising problem, however, is characterized by peaks that get sharper and sharper with the size of the system. The chemical example has localized peaks but these remain unaffected when the number of random walk steps is increased. This difference is again attributed to the different scaling.

(iii) The dependence of the relative stability of the quasistationary states on the size of the system is different in the two classes. We can get an estimate of the relative stability by considering the passage times from one well to the other and looking at their ratio.⁹ For the Ising-type system, as a consequence of the scaling

$$\frac{T(\text{stable} \rightarrow \text{metastable})}{T(\text{metastable} \rightarrow \text{stable})} \sim \exp[N\theta(1)], \quad (43)$$

and in the thermodynamic limit the stable state is actually infinitely more stable than the metastable state. In the chemical reaction example the ratio remains finite when the number of levels grows and depends only on the height difference in the potential surface.

(iv) The last point is closely related to the difference in the nature of the stationary bimodal distribution. The ratio of $P_e(\gamma)/P_e(\alpha)$ is given by [Eq. (10)]

$$P_e(\gamma)/P_e(\alpha) = \theta_\gamma/\theta_\alpha. \quad (44)$$

It is clear that when G_j is scaled as discussed in Sec. II, this ratio is of order $\exp[N \int_a^c \ln G(x) dx]$. Therefore, it is zero or infinite in the thermodynamic limit, depending on which state is more stable, i.e., the sign of

$$\int_a^c \ln G(x) dx.$$

Thus the "bimodal" distribution is effectively unimodal. For the reaction example, for which we do not have the same scaling property, this result does not hold, and the equilibrium distribution is truly bimodal in the stochastic space. Thus the differences in sharpness of the transition with the variation of external parameters are accounted for by the differences in scaling. It is interesting to notice that the bounds presented in Eq. (33) are such that their ratio gives exactly the ratio of the equilibrium probabilities of α and γ , as given by Eq. (44). This means that the bounds are reasonably good.

Finally, note that the form of the factor G_j is determined by the stationary distribution through the condition of detailed balance. It is interesting to observe that the stationary distribution holds a considerable amount of information on the temporal evolution of the system. This conclusion holds irrespective of whether the stationary distribution describes an equilibrium system or a nonequilibrium stationary state.

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APPENDIX A: SIMPLIFIED EXPRESSIONS FOR THE MEAN FIRST PASSAGE TIME

We consider a stochastic process defined by the birth and death master equation

$$\begin{aligned} \frac{dP_0}{dt} &= L_{10}P_1 - L_{01}P_0, \\ \frac{dP_1}{dt} &= L_{01}P_0 - (L_{10} + L_{12})P_1 + L_{21}P_2, \\ &\vdots \\ \frac{dP_N}{dt} &= L_{N-1,N}P_{N-1} - (L_{N,N-1} + L_{N,N+1})P_N. \end{aligned} \quad (A1)$$

Here the state 0 is a reflecting barrier whereas the state N is absorbing. We wish to evaluate the mean first passage time $\langle T(r, N) \rangle$ for a system started at a state r to arrive at the state N :

$\langle T(r, N) \rangle$ is given by⁷

$$\langle T(r, N) \rangle = \sum_{j=0}^N P_j^*, \quad (A2)$$

where P_j^* are the solutions of the following set of equations:

$$\begin{aligned} L_{01}P_0^* &= L_{10}P_1^*, \\ (L_{10} + L_{12})P_1^* &= L_{01}P_0^* + L_{21}P_2^*, \\ &\vdots \\ (L_{r,r-1} + L_{r,r+1})P_r^* &= L_{r-1,r}P_{r-1}^* + L_{r+1,r}P_{r+1}^* + 1, \\ &\vdots \\ (L_{N,N-1} + L_{N,N+1})P_N^* &= L_{N-1,N}P_{N-1}^*. \end{aligned} \quad (A3)$$

We start solving Eqs. (A3) recursively, setting

$$\begin{aligned} P_j^* &= \theta_j P_0^* \quad j = 0, 1, \dots, r, \\ P_j^* &= \vartheta_j P_0^* - \eta_j \quad j = r+1, r+2, \dots, N, \end{aligned} \quad (A4)$$

where θ_j , η_j will be determined by the equations. The first r equations will be satisfied if we choose

$$\begin{aligned} \theta_0 &= 1, \\ \theta_j &= G_0 G_1 \cdots G_{j-1}, \end{aligned} \quad (A5)$$

where

$$G_j \equiv L_{j,j+1}/L_{j+1,j}. \quad (A6)$$

The $r+1$ st equation gives

$$\eta_{r+1} = 1/L_{r+1,r}. \quad (A7)$$

And if we proceed to the next equation we get that the η_j 's satisfy the equations

$$\begin{aligned} L_{j+1,j}\eta_{j+1} &= (L_{j,j-1} + L_{j,j+1})\eta_j - L_{j-1,j}\eta_{j-1}, \\ j &= r, r+1, \dots, \end{aligned} \quad (A8)$$

which result in the following general expression for the η_j 's:

$$\begin{aligned} \eta_{r+k} &= \frac{1}{L_{r+k,r+k-1}} \left(1 + \frac{L_{r+k-1,r+k}}{L_{r+k-1,r+k-2}} \right. \\ &\quad \left. + \frac{L_{r+k-1,r+k}L_{r+k-2,r+k-1}}{L_{r+k-1,r+k-2}L_{r+k-2,r+k-3}} + \frac{L_{r+k-1,r+k}L_{r+k-2,r+k-1}L_{r+1,r+2}}{L_{r+k-1,r+k-2}L_{r+k-2,r+k-3}L_{r+1,r}} \right). \end{aligned} \quad (A9)$$

Equation (A9) can be rearranged to yield

$$\begin{aligned} \eta_{r+k} &= \frac{1}{L_{r+k-1,r+k}} G_{r+k-1} + \frac{1}{L_{r+k-2,r+k-1}} \\ &\quad \times G_{r+k-1}G_{r+k-2} + \cdots + \frac{1}{L_{r,r+1}} G_{r+k-1}G_{r+k-2} \cdots G_r \end{aligned} \quad (A10)$$

for every $k = 1, 2, \dots, N-r$. Thus,

$$\begin{aligned} \eta_{r+k} &= \frac{1}{L_{r+k-1,r+k}} \frac{\theta_{r+k}}{\theta_{r+k-1}} + \frac{1}{L_{r+k-2,r+k-1}} \frac{\theta_{r+k}}{\theta_{r+k-2}} \\ &\quad + \cdots + \frac{1}{L_{r,r+1}} \frac{\theta_{r+k}}{\theta_r}. \end{aligned}$$

P_0^* will be determined by the last equation,

$$(L_{N,N-1} + L_{N,N+1})(\theta_N P_0^* - \eta_N) = L_{N-1,N}(\theta_{N-1} P_0^* - \eta_{N-1}), \quad (A11)$$

i. e. ,

$$(L_{N,N-1} + L_{N,N+1})\theta_{N-1} \frac{L_{N-1,N} P_0^* - L_{N-1,N}\theta_{N-1}P_0^*}{L_{N,N-1}} = (L_{N,N-1} + L_{N,N+1})\eta_N - L_{N-1,N}\eta_{N-1}, \tag{A12}$$

but the rhs of Eq. (A11) is exactly equal to $L_{N+1,N}\eta_{N+1}$ [see Eq. (A8)] and thus we get

$$P_0^* = \eta_{N+1}/\theta_{N+1}. \tag{A13}$$

Our expression for $\langle T \rangle$, (A2), can now be rearranged [using (A4)] to the form

$$\langle T(r, N) \rangle = \sum_{j=0}^r \frac{\eta_{N+1}}{\theta_{N+1}} \theta_j + \sum_{j=r+1}^N \left(\frac{\eta_{N+1}}{\theta_{N+1}} \theta_j - \eta_j \right). \tag{A14}$$

Let us consider now each sum in (A14) separately. Define ψ_j ,

$$\begin{aligned} \psi_j = \frac{\eta_{N+1}}{\theta_{N+1}} \theta_j &= \frac{1}{L_{N+1,N}} \frac{1}{G_N G_{N-1} \cdots G_j} \\ &+ \frac{1}{L_{N,N-1}} \frac{1}{G_{N-1} \cdots G_j} + \frac{1}{L_{N-1,N-2}} \frac{1}{G_{N-2} G_{N-3} \cdots G_j} \\ &+ \cdots + \frac{1}{L_{r+1,r}} \frac{1}{G_r G_{r-1} \cdots G_j} \\ &= \frac{1}{L_{N+1,N}} \frac{\theta_j}{\theta_{N-1}} + \frac{1}{L_{N,N-1}} \frac{\theta_j}{\theta_N} + \cdots + \frac{1}{L_{r+1,r}} \frac{\theta_j}{\theta_{r+1}} \\ &= \frac{1}{L_{N,N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1,N}} \frac{\theta_j}{\theta_{N-1}} + \cdots + \frac{1}{L_{r,r+1}} \frac{\theta_j}{\theta_r} \end{aligned} \tag{A15}$$

$j = 0, 1, \dots, r,$

and define χ_j ,

$$\begin{aligned} \chi_j = \frac{\eta_{N+1}}{\theta_{N+1}} \theta_j - \eta_j &= \frac{1}{L_{N,N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1,N}} \frac{\theta_j}{\theta_{N-1}} + \cdots + \frac{1}{L_{r,r+1}} \frac{\theta_j}{\theta_r} \\ &- \frac{1}{L_{j-1,j}} \frac{\theta_j}{\theta_{j-1}} + \frac{1}{L_{j-2,j-1}} \frac{\theta_j}{\theta_{j-2}} + \cdots + \frac{1}{L_{r,r+1}} \frac{\theta_j}{\theta_r} \\ &= \frac{1}{L_{N,N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1,N}} \frac{\theta_j}{\theta_{N-1}} + \cdots + \frac{1}{L_{j,j+1}} \frac{\theta_j}{\theta_j} \end{aligned} \tag{A16}$$

$j = r+1, \dots, N.$

Our final expression is thus

$$\langle T(r, N) \rangle = \sum_{j=0}^r \psi_j + \sum_{j=r+1}^N \chi_j, \tag{A17}$$

$$\psi_j = \frac{1}{L_{N,N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1,N}} \frac{\theta_j}{\theta_{N-1}} + \cdots + \frac{1}{L_{r,r+1}} \frac{\theta_j}{\theta_r}, \tag{A17'}$$

$$\chi_j = \frac{1}{L_{N,N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1,N}} \frac{\theta_j}{\theta_{N-1}} + \cdots + \frac{1}{L_{j,j+1}} \frac{\theta_j}{\theta_j}. \tag{A17''}$$

If we consider now the reverse problem in which the state 0 is absorbing and N reflecting, we shall have

$$\langle T(r, 0) \rangle = \frac{\tilde{\eta}_0}{\tilde{\theta}_0} \sum_{j=0}^r \tilde{\theta}_j - \sum_{j=0}^{r-1} \tilde{\eta}_j, \tag{A18}$$

where

$$\tilde{\theta}_N = 1,$$

$$\tilde{\theta}_j = \frac{1}{G_{N-1} \cdots G_j}, \tag{A19}$$

$$\tilde{\eta}_{r-k} = \frac{1}{L_{r-k,r-k+1}} \left(1 + \frac{L_{r-k+1,r-k}}{L_{r-k+1,r-k+2}} + \cdots + \frac{L_{r-k+1,r-k} \cdots L_{r-1,r-2}}{L_{r-k+1,r-k+2} \cdots L_{r-1,r}} \right), \tag{A20}$$

$$\begin{aligned} \tilde{\eta}_{r-k} &= \frac{1}{L_{r-k+1,r-k}} \frac{1}{G_{r-k}} \\ &+ \frac{1}{L_{r-k+2,r-k+1}} \frac{1}{G_{r-k} G_{r-k+1}} + \cdots + \frac{1}{L_{r,r-1}} \frac{1}{G_{r-k} G_{r-k+1} \cdots G_{r-1}} \\ &= \frac{1}{L_{r-k+1,r-k}} \frac{\tilde{\theta}_{r-k}}{\tilde{\theta}_{r-k+2}} + \frac{1}{L_{r-k+2,r-k+1}} \frac{\tilde{\theta}_{r-k}}{\tilde{\theta}_{r-k+2}} + \cdots + \frac{1}{L_{r,r-1}} \frac{\tilde{\theta}_{r-k}}{\tilde{\theta}_r}. \end{aligned} \tag{A21}$$

We shall now rearrange Eq. (A18) and write it in the form

$$\langle T(r, 0) \rangle = \sum_{j=0}^{r-1} \tilde{\chi}_j + \sum_{j=r}^N \tilde{\psi}_j, \tag{A22}$$

$$\tilde{\chi}_j = \frac{\tilde{\eta}_0}{\tilde{\theta}_0} \tilde{\theta}_j - \tilde{\eta}_j, \tag{A23}$$

$$\tilde{\psi}_j = \frac{\tilde{\eta}_0}{\tilde{\theta}_0} \tilde{\theta}_j. \tag{A24}$$

Using Eq. (A21) we have

$$\tilde{\eta}_0 = \frac{1}{L_{1,0}} \frac{1}{G_0} + \frac{1}{L_{2,1}} \frac{1}{G_0 G_1} + \cdots + \frac{1}{L_{r,r-1}} \frac{1}{G_0 G_1 \cdots G_{r-1}}. \tag{A25}$$

Thus we get

$$\begin{aligned} \frac{\tilde{\eta}_0}{\tilde{\theta}_0} &= \frac{1}{L_{10}} G_{N-1} G_{N-2} \cdots G_1 + \frac{1}{L_{21}} G_{N-1} \cdots G_2 \\ &+ \cdots + \frac{1}{L_{r,r-1}} G_{N-1} G_{N-2} \cdots G_r. \end{aligned} \tag{A26}$$

Substituting (A26) and (A19) into (A24) results in

$$\tilde{\psi}_j = \frac{1}{L_{10}} \frac{\tilde{\theta}_j}{\tilde{\theta}_1} + \frac{1}{L_{21}} \frac{\tilde{\theta}_j}{\tilde{\theta}_2} + \cdots + \frac{1}{L_{r,r-1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_r}. \tag{A27}$$

Similarly, from (A26), (A19), (A21), and (A23) we get

$$\begin{aligned} \tilde{\chi}_j &= \frac{\tilde{\eta}_0}{\tilde{\theta}_0} \tilde{\theta}_j - \tilde{\eta}_j \\ &= \left(\frac{1}{L_{10}} \frac{\tilde{\theta}_j}{\tilde{\theta}_1} + \frac{1}{L_{21}} \frac{\tilde{\theta}_j}{\tilde{\theta}_2} + \cdots + \frac{1}{L_{r,r-1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_r} \right) \\ &- \left(\frac{1}{L_{j+1,j}} \frac{\tilde{\theta}_j}{\tilde{\theta}_{j+1}} + \frac{1}{L_{j+2,j+1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_{j+2}} + \cdots + \frac{1}{L_{r,r-1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_r} \right) \\ &\equiv \frac{1}{L_{10}} \frac{\tilde{\theta}_j}{\tilde{\theta}_1} + \frac{1}{L_{21}} \frac{\tilde{\theta}_j}{\tilde{\theta}_2} + \cdots + \frac{1}{L_{j,j-1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_j}. \end{aligned} \tag{A28}$$

In summary,

$$\langle T(r, 0) \rangle = \sum_{j=1}^{r-1} \tilde{\chi}_j + \sum_{j=r}^N \tilde{\psi}_j, \tag{A29}$$

$$\tilde{\chi}_j = \frac{1}{L_{10}} \frac{\tilde{\theta}_j}{\tilde{\theta}_1} + \frac{1}{L_{21}} \frac{\tilde{\theta}_j}{\tilde{\theta}_2} + \cdots + \frac{1}{L_{j,j-1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_j}, \tag{A29'}$$

$$\tilde{\psi}_j = \frac{1}{L_{10}} \frac{\tilde{\theta}_j}{\tilde{\theta}_1} + \frac{1}{L_{21}} \frac{\tilde{\theta}_j}{\tilde{\theta}_2} + \cdots + \frac{1}{L_{r,r-1}} \frac{\tilde{\theta}_j}{\tilde{\theta}_r}. \tag{A29''}$$

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