Time scale of thermally activated diffusion in random systems: A new law of thermal activation

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Exact time scales are obtained for a class of stochastic models of thermally activated diffusion in random systems with a one-dimensional quantum reaction coordinate. The results are valid at any temperature. At low temperatures various forms of the thermal activation law of Arrhenius emerge, the dominant time scale of the diffusion depending on the temperature T according to $T^p \exp(A/k_BT)$, where A is the activation energy and p an exponent depending on the details of the models. These correspond to different bounded energy spectra for the randomly selected energy levels along the reaction coordinate. As an example we consider the Wigner semicircular distribution of eigenvalues of large random matrices. Another example considered is a Gaussian distribution of energy levels, and in this case a new thermal-activation law is obtained, having the form $\exp[B^2/(k_BT)^2]$, where B is proportional to the width of the distribution. This form has recently been found in Monte Carlo experiments on large Ising-spin-glass models by Young.

Recently it has become feasible to give exact evaluations of the dominant time scale in stochastic models of such processes as Monte Carlo experiments and classical diffusion.[1-3] These models are described by the master equation for the evolution of the probabilities $\{W_\alpha\}$ of occupation of a set of quantum states labeled by the index α:

$$\frac{d}{dt}W_\alpha = -\sum_\beta L_{\alpha\beta}W_\beta, \quad \sum_\alpha W_\alpha = 1 . \tag{1}$$

Here $\{L_{\alpha\beta}\}$ are the elements of the stochastic matrix L, and satisfy

$$\sum_\alpha L_{\alpha\beta} = 0, \quad L_{\alpha\beta} \le 0 \text{ for } \alpha \ne \beta . \tag{2}$$

The time scale for relaxation to equilibrium $\{W^0_\alpha\}$ depends on the eigenvalues of L. The conditions (2), which derive from the interpretation of the elements of L as conditional transition probabilities per unit time, imply that it has only non-negative eigenvalues, and at least one is equal to zero, i.e., $l_1 = 0$. The dominant time scale is then given by the smallest of the remaining eigenvalues, i.e., $\tau_2 = 1/l_2$. Since the eigenvalue l_2 resides inside the spectrum of L, it has only recently been considered[1] how to estimate τ_2 exactly, in the form of upper and lower bounds. Hence, while the existence of the eigenvalue $l_1 = 0$ is sufficient to establish the existence of a stationary solution $\{W^0_\alpha\}$, one needs to know l_2 to estimate how long it takes to reach it. The conventional bound on l_2 coincides with $l_1 = 0$, and hence does not provide a finite upper bound on τ_2.

In the present paper we shall apply the new finite upper bound $\tau_2 \le \tau$, which is available, so far, only when L is tridiagonal. This means that, in the models we may consider, a kinetics corresponding to an essentially one-dimensional chain of quantum states must be selected by the system, which will serve as a "quantum reaction coordinate." We refer to this principle as "optimal network kinetics," which is explained in more detail elsewhere.[4]

Suppose the system is in contact with a reservoir keeping the temperature equal to T, and let the quantum states have energies $\{E_\alpha\}$: The condition of detailed balance

$$L_{\alpha\beta}W^0_\beta = L_{\beta\alpha}W^0_\alpha , \tag{3}$$

where then

$$W^0_\alpha = e^{-E_\alpha/k_BT}/Z, \quad Z = \sum_\alpha e^{-E_\alpha/k_BT} \tag{4}$$

is sufficient to assure that the equilibrium state is reached, but of course in itself does not establish how long it takes.[1]

The nature of the system then defines the stochastic model in terms of the sets of parameters $\{E_\alpha\}$ and the elements of L. We shall discuss models in which the energies are random variables, sampled, for each quantum state along the reaction coordinate, from a distribution with probability density $\phi(E)$, normalized for each state: $\int dE\, \phi(E) = 1$. The stochastic process then corresponds to thermally activated hopping between random energy levels.[4]

In Ref. 3 we discuss models in which a strong correlation was assumed to exist between adjacent energy levels, forming a continuous potential in the classical limit, whereby the stochastic model represents a classical diffusion process with a continuous reaction coordinate. Of course, for a quantum reaction coordinate, the distinction between hopping and diffusion is merely formal. But in the limit of an infinite sequence of states the results are qualitatively different in the two cases, which are both of considerable physical interest.

Let

$$H_{\alpha,\beta}=\sum_{\gamma=\alpha+1}^{\gamma=\beta} W_\gamma^0 \ . \tag{5}$$

When a sufficient number of states along the reaction coordinate are sampled in this sum, we assume a form of ergodicity which implies that for $|\beta-\alpha|\to\infty$ (cf. Ref. 4)

$$H_{\alpha,\beta}\to(\beta-\alpha)\int_{-\infty}^{\infty} dE\,\phi(E)\frac{e^{-E/k_BT}}{Z} \ . \tag{6}$$

This is obviously true for independent random energies E_γ in W_γ^0. However, it is of interest to note that it may still hold if the E_γ display certain forms of correlations, as may be the case in realistic systems.

For example, in a Monte Carlo sequence of spin flips in an Ising model the energies differ at most by the maximum energy change possible due to the reversal of a single spin, and this is generally much smaller than the total energy. So a correlation exists until a large number of spins have been flipped, even if the spin-interaction energies are random.

The class of models of random systems for which the results of the present work are valid can then be defined by requiring the validity of (6). It has been shown that if the energies E_γ are the eigenvalues of members of certain ensembles of large random matrices,[5,6] then for almost every *individual* matrix the condition (6) holds when $\phi(E)$ is chosen as the *ensemble* level density for the given class of random matrices, in the limit when they become infinitely large.[7–9] Thus, the E_γ need not be independent as long as they are sampled with equal weight throughout the spectrum of the given random matrix.

If we assume initially that there are g quantum states along the reaction coordinate, reserving the limit $g\to\infty$ for later, then the partition function becomes

$$Z=g\int_{-\infty}^{\infty} dE\,\phi(E)e^{-E/k_BT} \ , \tag{7}$$

as soon as g is large enough to bring (6) into effect.

In order to make the models definite we shall assume about the matrix of transition probabilities the following parametrization. Let, for $\alpha\neq\beta$, $p_{\alpha\beta}=p_{\beta\alpha}$, and let $\{E_{\alpha\beta}\}$ be a set of parameters of dimension energy. For $\alpha\neq\beta$, then

$$L_{\alpha\beta}=-p_{\alpha\beta}e^{-E_{\alpha\beta}/k_BT} \ . \tag{8}$$

For $\alpha=\beta$ the elements are given by Eq. (2). Detailed balance (3) then implies the constraint

$$E_{\alpha\beta}-E_{\beta\alpha}=E_\alpha-E_\beta \ . \tag{9}$$

Of course, this is not sufficient to determine all the parameters. While our result could be stated for any choice of transition probabilities, it is not in general expressible in elementary terms. In order to facilitate this, let us consider a simpler set of transition probabilities, defined according to

$$E_{\alpha\beta}=rE_\alpha+(r-1)E_\beta, \quad p_{\alpha\beta}=\frac{1}{\tau_0 Z^{2r-1}} \ . \tag{10}$$

Here r is a real, non-negative parameter. Then, for $\alpha\neq\beta$, the matrix L is given by

$$L_{\alpha\beta}=-\frac{1}{\tau_0}(W_\alpha^0)^r(W_\beta^0)^{r-1} \ . \tag{11}$$

This choice is simply for definiteness and convenience. By considering models with different values of r, such as $r=\frac{1}{2}$ or $r=1$, we can draw conclusions about the nature of the influence which the transition probabilities have on the resulting time scale, irrespective of how the energy levels are arranged. Models of such considerable interest as those of Metropolis *et al.* and Glauber,[10] favored in Monte Carlo experiments, have the same functional form as Eq. (11) for $r=\frac{1}{2}$ in that the transition probability depends on the energy difference $E_\beta-E_\alpha$, and are physically equivalent to this case, except for being slightly more complicated to treat analytically.[4] In the models defined by Eq. (11) and the $\phi(E)$ to be given in the following, the resulting time scale can be expressed exactly in terms of standard functions.

The upper bound on the time scale is given by[1]

$$\tau=\sum_{\alpha=1}^{\alpha=g-1}\frac{H_{0,\alpha}H_{\alpha,g}}{|L_{\alpha\alpha+1}|W_{\alpha+1}^0}=\tau_0\sum_{\alpha=1}^{\alpha=g-1}\frac{H_{0,\alpha}H_{\alpha,g}}{(W_\alpha^0W_{\alpha+1}^0)^r} \ . \tag{12}$$

Introducing the Laplace transform of ϕ, where $\beta=1/k_BT$ (not to be confused with the index, of course),

$$\Phi(\beta)=\int_{-\infty}^{\infty} dE\,\phi(E)e^{-\beta E} \ , \tag{13}$$

we have, according to Eqs. (6) and (7),

$$H_{0,\alpha}=\alpha\Phi(\beta)/Z \ , \tag{14}$$

$$H_{\alpha,g}=(g-\alpha)\Phi(\beta)/Z \ , \tag{15}$$

$$Z=g\,\Phi(\beta) \ . \tag{16}$$

The ergodicity (6) implies that now the sum in Eq. (12), depending on the energies, due to the energy dependence in the transition probabilities induced (along with the temperature) by the detailed balance requirement (3), is also convertible to an integral in the limit $g\to\infty$. In the model (11) this follows because the exponential dependence is similar (as will appear) under reasonable assumptions about the spectral density $\phi(E)$. Furthermore, it may be noted here that in some cases the upper limit τ may become infinite, i.e., the dominant time scale may be infinitely long. Also this conclusion would be physically significant, indicating that equilibrium cannot be reached in finite time. This could be a consequence of having energies with $\phi(E)$ which would make the integral version of (12) nonexistent.

These considerations, as well as those in the following of a similar nature, all relate to the laws of large numbers.[11] Our concept of ergodicity, therefore, has a rigorous foundation. Decisions about the behavior in probability of the sums in (6) and (12) as $g\to\infty$ can be reached, for every *individual* realization of the randomly constructed structure, by an analysis of $\phi(E)$.[4] There is no need for any subsequent averaging over any *ensemble* of such structures (which is known to produce potentially ambiguous results). The time scale τ which we shall derive applies with probability one to any individual ran-

dom structure, as soon as g is sufficiently large (cf. Appendix). The reason that we do not let $g\to\infty$ immediately will become clear in the following.

The probability density of the random variable $E_\alpha+E_{\alpha+1}$ in (12) is the convolution of ϕ with itself, assuming that E_α and $E_{\alpha+1}$ are independent (but cf. Ref. 4):

$$\psi(E_\alpha+E_{\alpha+1})=\int_{-\infty}^{\infty} dE\,\phi(E)\phi(E_\alpha+E_{\alpha+1}-E)\ . \tag{17}$$

Its Laplace transform is

$$\Psi(\beta)=\Phi(\beta)^2\ . \tag{18}$$

Finally, in order to evaluate (12) we note that

$$\sum_{\alpha=1}^{\alpha=g-1}\alpha(g-\alpha)=\tfrac{1}{6}(g+1)g(g-1)\simeq\tfrac{1}{6}g^3\ .$$

We then find

$$\tau=\tfrac{1}{6}\tau_0 g^3[\Phi(\beta)/Z]^2\int_{-\infty}^{\infty}dE\psi(E)e^{r\beta E}Z^{2r}$$

or

$$\tau=\tfrac{1}{6}\tau_0 g^{2r+1}[\Phi(\beta)^r\Phi(-r\beta)]^2\ . \tag{19}$$

In this result, if τ is to be finite, then the two-sided Laplace transforms must exist, which means that $\phi(E)$ must vanish sufficiently rapidly as $E\to\pm\infty$ to balance the exponential in (13). If τ becomes infinitely large it may imply that in the random systems arbitrarily high energy levels somewhere along the reaction coordinate become too frequent to allow a finite value of τ_2. It should be noted, however, and examples will be given in the following, that we do not have to completely exclude such high energies from $\phi(E)$, only to assume that they are not too heavily represented to prevent a finite τ. But in any case the result we obtain for τ is meaningful. The possibility that states of large energy along the reaction coordinate may break it up is due to the detailed balance requirement which introduces the temperature T into the elementary transition probabilities in the models. This condition is not necessary in order to obtain results such as the upper bound on τ_2 with the present methods,[1] but simplifies the investigation and is physically well motivated. If the chain of quantum states in a model effectively breaks into smaller pieces which do not communicate for this reason, then one may consider systems corresponding to models with energy levels belonging only to one such effectively connected piece at a time, and for each obtain its individual τ by means of the appropriately modified $\phi(E)$ and (19).

With models based on the canonical detailed balance conditions (3) and (4), the states are recurrent for finite g, but may or may not become null-recurrent when $g\to\infty$.[1] If the elements of L are modified, say such as to create an absorbing state at the end, $L_{g-1g}=0$ and $L_{gg-1}\neq 0$, then the equilibrium is rather $W_g^0=1$, and $W_\alpha^0=0$ for $1\le\alpha\le g-1$, and the latter states are transient. The theory may then be applied to problems of the first-passage time scale,[12] where the state to be passed is g, after which event no return is possible. The time τ is an upper bound on the longest time that may lapse before the passage, and can be compared with the existing expressions for the mean first-passage time.[13]

The case of diffusion, which we consider in the present work, is distinct from the first-passage case and the system may return to any state arbitrarily often in the long run, except under the special circumstances discussed above. Whereas in continuous potentials used to describe reactions that terminate the stochastic process once the system reaches the absorbing state (more generally, once it leaves the class of transient states considered), the first-passage criterion may be most relevant; in the present models of diffusion in random systems one cannot identify any particular state for which a first-passage would be physically significant. This is especially the case in optimal network kinetics, since the network can be expected to have a high degree of connectedness. However, the discussion of the first-passage problem from a class of transient states with random structure seems feasible in the present approach.

I. BINARY MODELS

When $T\to 0$, $\beta\to+\infty$, $\Phi(\beta)$ is dominated by the parts of $\phi(E)$ of lowest energy, while $\Phi(-r\beta)$ is dominated by the parts of highest energy. Thus, the simplest model of $\phi(E)$ only contains two energy levels $E_{\rm low}$ and $E_{\rm high}$ represented with weights w_{low} and $w_{\rm high}$:

$$\phi(E)=w_{\rm low}\delta(E-E_{\rm low})+w_{\rm high}\delta(E-E_{\rm high})\ . \tag{20}$$

The leading terms as $T\to 0$ then become

$$\Phi(\beta)\sim w_{\rm low}e^{-\beta E_{\rm low}}\ ,$$

$$\Phi(-r\beta)\sim w_{\rm high}e^{r\beta E_{\rm high}}\ .$$

This would also be the case in models with a spectral weight of $\phi(E)$ at intermediate levels as long as $E_{\rm low}$ and $E_{\rm high}$ are separated from them by a finite gap. In the latter case $w_{\rm low}+w_{\rm high}<1$. Thus, the leading term of τ becomes

$$\tau\sim\tfrac{1}{6}\tau_0 g^{2r+1}(w_{\rm low}^r w_{\rm high})^2 e^{\beta A}\ , \tag{21}$$

where

$$A=2r(E_{\rm high}-E_{\rm low})\ . \tag{22}$$

This result displays the thermal-activation law of Arrhenius[14] with activation energy A. In general, this law implies the existence of a dominant time scale depending on the temperature according to

$$\tau\sim f(T)e^{\beta A}\ \text{ for }\ T\to 0\ , \tag{23}$$

where $f(T)$ is a less singular function than the exponential in the limit $T\to 0$. It also emerges in nonrandom systems,[2,3] and can be interpreted, as is well known, in terms of energy barriers along the reaction coordinate of height related to the activation energy A. The exact relation, however, also depends on the nature of the transition probabilities, which is evident in (22) because of the presence of the parameter r.

In particular, for $r=\frac{1}{2}$ we get $A=E_{\rm high}-E_{\rm low}$. This result distinguishes itself from the form of the activation

energy in nonrandom systems.[2] Ordinarily A is the energy difference between the energy at the summit of a barrier configuration and that of a "metastable" local energy minimum, which may not be as low as E_{low}, provided, of course, the model has such energy levels at all. However, the randomness implies that on both sides of the summit of a barrier along the reaction coordinate there must be states with energies as small as the lowest one, E_{low}.

Letting $w_{\text{low}}=w_{\text{high}}=\frac{1}{2}$ and $E_{\text{high}}=-E_{\text{low}}=\Delta$ in (20) the result at arbitrary temperature is

$$\tau=\tfrac{1}{6}\tau_0 g^{2r+1}[\cosh^r(\beta\Delta)\cosh(r\beta\Delta)]^2 . \tag{24}$$

Now consider the dependence on the size g. It is physically most reasonable to assume that when $g\to\infty$ then τ_0 depends on g in such a way that the transition probabilities $p_{\alpha\beta}$ remain finite. According to (10) and (16) we may then assume that D_0 is a finite parameter in this limit, and defined by

$$D_0=g^{1-2r}/\tau_0 . \tag{25}$$

From (21) we then conclude that $\tau\sim g^2$ as $g\to\infty$, which is a diffusive behavior.[3] The system will never reach equilibrium, but its evolution will correspond to diffusion with diffusion constant

$$D^*=g^2/6\tau\sim D_0(w_{\text{low}}^r w_{\text{high}})^{-2}e^{-A/k_BT} , \tag{26}$$

which remains finite. Due to the randomness the energy barriers occur with uniform probability throughout the length of the reaction coordinate. They would not in general have identical shapes, but as $T\to 0$ only their heights matter. These barriers are "equivalent" in this sense, and a further analysis employing the results of Ref. 1 shows that in such cases there will be several time scales besides τ_2 which obtain the leading low-T form. This has the consequence that in the limit τ_2 does not become equal to τ, but differs by a numerical factor which is, however, not of the order g but of the order 1. In elementary diffusion, which can be solved exactly for all time scales, this factor is $\lim_{g\to\infty}(\tau/\tau_2)=\pi^2/6$. We conjecture that in the present random case there is a similar relation between the times scales and the diffusion constant as in the conventional diffusion processes.[3] The basis of this significant aspect is that for all models in which $L_{\alpha\alpha+1}L_{\alpha+1\alpha}\neq 0$ it is known[15] that the eigenvalues of L are all simple. Hence, the time scales $\tau_2, \tau_3, \ldots$ do not coincide, even though they assume the same leading $T\to 0$ form. This formation of a "band" of dominant time scales, containing as many of these as there are equivalent barriers, means that their sum τ (cf. Ref. 1) is not proportional to their number, but rather to a moderate number such as the $\pi^2/6$ of the diffusion models. Therefore, in most contexts it would be quite reasonable to regard the time scale τ and the diffusion constant D^* as the physically relevant results, considering the strong temperature dependence of the law of Arrhenius.

II. GAUSSIAN MODEL

Consider next the case of a Gaussian density:

$$\phi(E)=\frac{1}{\sqrt{2\pi}w}e^{-E^2/2w^2} , \tag{27}$$

where w is the energy variance. In the absence of detailed information about the energy levels this would be a most plausible assumption on which to base a model, and it also occurs in some ensembles of random matrices.[5,9] Its two-sided Laplace transform is

$$\Phi(\beta)=e^{(w^2/2)\beta^2} .$$

We thus find, at any temperature

$$\tau=\tfrac{1}{6}\tau_0 g^{2r+1}e^{(r+r^2)w^2/(k_BT)^2} . \tag{28}$$

This is a new thermal-activation law, distinguished from the Arrhenius law (23) by its much stronger temperature dependence.

In Monte Carlo studies of large, two-dimensional Ising-spin-glass models Young found[16] a temperature dependence of the relaxation time of precisely the form (28) (in zero magnetic field). As is indicated by its dependence on the parameter r, this form apparently is rather independent of details in the transition probabilities. Since our[4] result [Eq. (28)] is also relevant in models with transition probabilities of the forms of Metropolis *et al.* and Glauber, we may interpret Young's result in the following way. In a sequence of Monte Carlo spin flips the Ising-spin-glass energy forms a random succession which in the long run becomes ergodic in the present sense, due to the randomness of the Ising coupling constants (here taking values ± 1 randomly for nearest neighbors). The thermal bias introduced by the detailed balance in the transition probabilities should then cause the system to perform a hopping in the spin configuration space which preferably, at low temperatures, will take it from one local energy minimum to another across a random barrier along a path of comparatively low energies. This could be regarded as a manner of forming an essentially one-dimensional quantum reaction coordinate, or a more or less uniform network of such paths. It also implies that the energy spectrum $\phi(E)$ on such a network, selected by thermal bias, will be rather different from the spectrum of the complete set of states of the Ising model.[17] Particularly, spin configurations with larger energies than those which occur on the network would be unlikely to occur during such a run. It might, therefore, be realistic to consider the network energy density as a Gaussian [Eq. (27)], in which large energies are relatively weakly represented, although not absent. Further details were discussed in Ref. 4.

III. SEMICIRCULAR MODELS

Suppose that the energies are eigenvalues of large random matrices, of dimension N. For an ensemble of such Hermitian matrices it follows that $\phi(E)$ is the Wigner distribution[7,8]

$$\phi(E)=\frac{2}{\pi\Delta}\left[1-\frac{E^2}{\Delta^2}\right]^{1/2} \quad \text{for } |E|\leq\Delta . \tag{29}$$

Here $\Delta^2=4N\delta^2$, where δ^2 is the second moment of the distribution of elements of the matrices in the ensemble.[18,19]

Since our evaluation of τ will be feasible for a more

general class of densities $\phi(E)$, including (29), we shall consider

$$\phi(E)=\frac{1}{\pi\Delta}\frac{(2^{\mu}\mu!)^2}{(2\mu)!}\left[1-\frac{E^2}{\Delta^2}\right]^{\mu-1/2} \quad \text{for } |E|\leq\Delta\ , \tag{30}$$

normalized for $\mu>-\frac{1}{2}$, with $\phi(E)=0$ elsewhere. For $\mu=1$ it is the Wigner density (29), for $\mu=\frac{1}{2}$ it is the uniform density $\phi(E)=\frac{1}{2}\Delta$, for $\mu=0$ it is a random-phase sampling of a sinusoidal energy with amplitude Δ, while for $\mu\to\infty$ it becomes $\delta(E)$. Thus,[20]

$$\Phi(\beta)=\mu!\left|\frac{2}{\beta\Delta}\right|^{\mu}I_{\mu}(|\beta\Delta|),\quad \mu>-\tfrac{1}{2}\ .$$

From (19) we then find

$$\tau=\tfrac{1}{6}\tau_0 g^{2r+1}r^{-2\mu}\left[\mu!\left[\frac{2}{\beta\Delta}\right]^{\mu}\right]^{2(r+1)}$$

$$\times[I_{\mu}(\beta\Delta)^{r}I_{\mu}(r\beta\Delta)]^2\ . \tag{31}$$

This is valid at any temperature. Its leading low-T form is obtained from

$$I_{\mu}(x)\sim e^{x}/\sqrt{2\pi x}\ ,$$

and is

$$\tau\sim\tfrac{1}{6}\tau_0 g^{2r+1}\frac{(\mu!)^{2(r+1)}}{(4\pi)^{r+1}r^{2\mu+1}}\left[\frac{2k_BT}{\Delta}\right]^{(2\mu+1)(r+1)}e^{4r\Delta/k_BT}\ . \tag{32}$$

For example, if $r=\frac{1}{2}$ and $\mu=1$, the Wigner distribution implies

$$\tau=\tfrac{4}{6}\tau_0 g^2\left[\frac{2}{\beta\Delta}\right]^3 I_1(\beta\Delta)I_1(\tfrac{1}{2}\beta\Delta)^2\ , \tag{33}$$

while for $\mu=\frac{1}{2}$ the uniform distribution implies

$$\tau=\tfrac{1}{6}\tau_0 g^{2r+1}\frac{1}{r^2}(\beta\Delta)^{-2(r+1)}[\sinh^{r}(\beta\Delta)\sinh(r\beta\Delta)]^2\ . \tag{34}$$

The low-temperature form with these continuous densities also produces the law of Arrhenius, the activation energy being $A=4r\Delta$, i.e., $2r$ times the width of $\phi(E)$ as in Eq. (22). However, in the present cases it is seen how the continuity near the edges brings various versions of temperature-dependent functions $f(T)$ of (23) into τ. These are powers of T, and depend on the nature of the singularity at the edges of the spectrum. They are also present in the case of diffusion in a continuous classical potential,[3] the power depending on the nature of the model as in the present random case. These extra temperature dependences, apart from the almost universal and model-independent exponential, give rise to convexity in the so-called Arrhenius plot, which is shown in Fig. 1 for a selection of our present $r=\frac{1}{2}$ models. In the case of Sec. I the curve is straight at low enough temperature, and the curvature is only seen at high temperatures. On the contrary, in both of the cases with continuous $\phi(E)$ considered in Secs. II and III the curvature persists to the lowest temperatures, and in the Gaussian model it is particularly pronounced. This dependence corresponds well with the Monte Carlo experiment on the random Ising spin glass,[16] while the somewhat weaker curvature of the models in Sec. III, due to the power-law dependence of $f(T)$, resembles the temperature dependence seen in the viscosity of glass-forming liquids.[21] It seems reasonable to conclude from the present study that such curvature can be expected to continue to $T=0$, and is a universal feature which may be particularly pronounced in random systems with continuous energy spectra.

The discrepancy between the Monte Carlo simulations in the two-dimensional Ising-spin-glass model of Young[16,22] and of McMillan[23] can easily be interpreted in the present context. In the first instance the Gaussian model of Sec. II applies accurately, while in the second experiment the data appear more like the semicircular models of Sec. III with a relatively large μ (cf. Fig. 1). In fact, for large μ, the density (30) with $\Delta=\sqrt{2\mu-1}w$ ap-

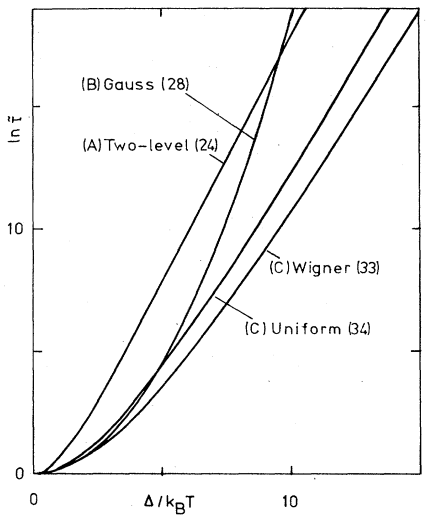

FIG. 1. Diffusion time scale $\tilde{\tau}=6\tau/\tau_0 g^{2r+1}=D_0/D^*$ in models with transition probabilities of $r=\frac{1}{2}$ in (11) in Arrhenius plot $\ln\tilde{\tau}$ vs Δ/k_BT, where 2Δ is the width of the random energy distribution $\phi(E)$. Curves are labeled according to the models defined in the text, and the plotted functions are expressions (24), (28), (33), and (34). Various degrees of curvature are present in the $T\to0$ limit, particularly in the Gaussin model where we used $w=\Delta/2$. The straight line obtained with the model in Sec. I corresponds to the law of Arrhenius with no temperature-dependent factor $f(T)$ in (23). The result for the Gaussian model is not expressible in this form, and is a new thermal-activation law appropriate to certain random models. It is notable that until the temperature becomes quite low the models with bounded spectra of Sec. III follow a rather similar parabolic temperature dependence, but then at the lowest temperatures assume a power-law form for $f(T)$, the exponent depending on details of the model. Thus, in (33) it is $\frac{9}{2}$, while in (24) it is zero. In these models, and also in the uniform case (34), the activation energy is the same $A=2\Delta$. It can be seen that the illusion of a straight curve at low T in the cases with a nonvanishing power in $f(T)$ can be quite deceptive, and the slope does not provide the correct activation energy corresponding only to the slope of the curve of (24).

proaches the Gaussian (27) asymptotically, except for the slightly weaker wings near the cutoffs at $\pm\Delta$. In a finite model, the spectrum $\phi(E)$ must end at some finite energy, such as Δ, and the contingent nature of the effect may therefore well cause discrepancies such as those reported.

Recent studies of large three-dimensional Ising-spin-glass models[24] have shown that the kinetics depends significantly on the dimensionality. This is quite consistent with the ideas behind the present work, since the nature of the optimal network is structural.[4] Although the precise low-temperature dependence remains undecided so far, it seems to require spectra $\phi(E)$ different from those considered here. The same can be said about the time scales of the real spin glasses,[25] and many other glass-forming systems. But in these cases we have found that certain simple and plausible premises lead to a spectrum $\phi(E)$ which implies the observed Vogel-Fulcher temperature dependence.

APPENDIX

The weighted sum of random variables in (12) is proportional to

$$Y=\sum_{\alpha} f_\alpha X_\alpha ,$$

where

$$X_\alpha = e^{r\beta(E_\alpha+E_{\alpha+1})}, \quad f_\alpha=\frac{1}{g}H_{0,\alpha}H_{\alpha,g} .$$

The density $\psi(E)$ of $E=E_\alpha+E_{\alpha+1}$ derives from ϕ, so the $\{X_\alpha\}$ are identically distributed, but not independent, even if the $\{E_\alpha\}$ are. One must prove that as $g\to\infty$,

$$Y \underset{\to}{p} Y_0=\sum_{\alpha} f_\alpha X_0 ,$$

where

$$X_0=\int_{-\infty}^{\infty} dE\psi(E)e^{r\beta E} .$$

Let each X_α be correlated with at most n variables among the set $\{X_\alpha\}$, including itself, and denote this subset $\mathscr{B}_\alpha$. Let σ_0^2 be the variance of the X_α with ψ. By the Cauchy-Schwarz inequality,

$$|\operatorname{cov}(X_\alpha,X_\beta)| \le \sigma_0^2, \quad \text{if } \beta\in\mathscr{B}_\alpha$$
$$=0, \quad \text{if } \beta\notin\mathscr{B}_\alpha .$$

The variance σ^2 of Y then satisfies the inequality

$$\sigma^2\le\sigma_0^2\sum_{\alpha}\sum_{\beta\in\mathscr{B}_\alpha} f_\alpha f_\beta .$$

By definition of $H_{\alpha,\beta}$

$$0\le f_\alpha\le\frac{1}{g} ,$$

hence

$$\sigma\le\sigma_0(n/g)^{1/2} .$$

According to (14)—(16),

$$f_\alpha \underset{\to}{p} \frac{\alpha}{g^2}\left[1-\frac{\alpha}{g}\right] \Longrightarrow \sum_{\alpha} f_\alpha \underset{\to}{p} \tfrac{1}{6}\left[1-\frac{1}{g^2}\right]\simeq\tfrac{1}{6} ,$$

so $Y_0=\frac{1}{6}X_0$. Consequently $\sigma\to 0$ as $g\to\infty$, provided $\sigma_0<\infty$ and $n/g\to 0$. By Chebyshev's inequality then $Y\to Y_0$ with probability one. It is conceivable that this is also true if σ_0 does not exist, as long as X_0 does and the correlations are short range in the sense $n/g\to 0$. Thus,

$$\tau=\tau_0 g Z^{2r} Y\sim\tfrac{1}{6}\tau_0 g^{2r+1}\Phi(\beta)^{2r}X_0 .$$

The locations of the correlation sets $\{\mathscr{B}_\alpha\}$ are arbitrary, which is particularly reassuring with optimal network kinetics.

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