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ARTICLES

Critical scaling behavior in the activated-barrier-crossing problem

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We study the activated-barrier-crossing (ABC) problem using the Hamiltonian approach with general memory friction kernels and for a parabolic barrier joined to an infinite wall. We solve the problem using the Grote-Hynes (GH) theory and the more recent Pollak-Grabert-Hänggi (PGH) approach. We show that the singular behavior of the rate for large memory correlation times is an example of critical phenomena. We determine all the relevant critical exponents in different regimes and explicitly show that the rate has a scaling behavior. We verify that the universality of exponents and amplitudes is applicable in both the GH and the PGH solutions. Studying the ABC problem with techniques borrowed from critical phenomena reveals its rich mathematical structure and points out the ways in which one may discover the critical behavior of this problem experimentally.

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I. INTRODUCTION

The problem of activated barrier crossing (ABC) has attracted a great deal of interest recently [1,2]. Kramers pioneered an approach to this problem based on the Langevin equation [3] using a static (or Markovian) friction γ, which is proportional to the viscosity of the medium. The assumption of Markovian friction means that the escaping particles are moving slowly compared with the rapid fluctuations exerted on them by the heat bath. Kramers solved this problem in both the small and the large damping limits. In the small damping limit, the motion is almost conservative, the rate limiting step being the gaining of sufficient energy by the particles to reach the barrier top. This is called the energy diffusion limit and the rate is proportional to γ. In the high damping limit, the escaping particles are in equilibrium with the heat bath in the potential well region and the rate limiting step is the passage over the barrier. This is called the spatial diffusion limit and the rate is proportional to $1/\gamma$. In the case when the potential is a parabolic barrier, Kramers obtained an exact solution to the ABC problem for Markovian friction. The rate equation for this case is usually called his intermediate to high damping result. Kramers's results have now been generalized in many different directions including memory friction [4].

If the friction term in the Langevin equation involves memory, then this equation is called a generalized Langevin equation. Grote and Hynes [4] solved the problem exactly in this case for a purely parabolic barrier. Later, van der Zwan and Hynes applied the Grote-Hynes (GH) approach to their model for a dipole isomerization reaction rate in polar solvents [5]. They found that in the regime of long solvent response times, the reaction rate had singular aspects which could be described in terms of simple power laws.

Very recently we found [6] that this behavior is more general than the van der Zwan–Hynes model and shows up whenever the memory relaxation time τ in the ABC problem is sufficiently large. We showed that the singular behavior can be understood easily from the point of view of critical phenomena. We also demonstrated that the escape rate can have scaling properties typically associated with such phenomena. It is well known from the study of critical phenomena [7] that whenever a characteristic length or time scale in a problem becomes very large, scaling and universality arise automatically. Scaling means that the various physical quantities can be represented as functions of scaled parameters. This usually implies new relations between critical exponents [8]. Universality means that the exponents depend on very few relevant parameters of the system and certain combinations of critical amplitudes also depend on few relevant parameters [8].

The purpose of this paper is to provide more details concerning our previous calculations regarding the parabolic barrier with an infinite wall. Details of other potentials will be published separately in the future. In Sec. II we briefly introduce the model and review the known results. In Sec. III we study the GH limit of the ABC theory, where the barrier has an exact parabolic shape. We illustrate how and why one uses scaling and universality using the case of an exponential memory friction. In Sec. IV we generalize the memory friction in the GH theory in order to reveal the dependence of various exponents on the form of the memory friction. In Sec. V we introduce our more general scaling hypothesis. In Sec. VI we solve the perfectly reflecting wall (PRW) model using the Pollak-Grabert-Hänggi (PGH) approach. In Sec. VII we study this solution in the scaling limit and obtain the scaling functions. In Sec. VIII we discuss, from the point of view of scaling, the piecewise parabolic potential studied in detail by Pollak, Grabert, and Hänggi. We find that this potential and the PRW have the same set of exponents and combinations of critical amplitudes. Concluding remarks are provided in Sec. IX.

II. MODEL AND PREVIOUS RESULTS

In this section we introduce our model and review previous results. We are concerned with the ABC problem in one dimension, where the damping force has memory. In the Langevin approach to this problem, this means that the damping term $-\gamma v$, where v is the velocity of the escaping particle, is replaced by $-\int_0^t dt'\zeta(t-t')v(t')$, $\zeta(t)$ being the memory friction kernel (MFK).

Typically, one deals with an MFK of the form

$$\zeta(t)=\frac{\gamma}{\tau}g\left[\frac{t}{\tau}\right], \tag{1}$$

where τ is a relaxation time such that, for $t \gg \tau$, the value of $\zeta(t)$ becomes very small, ultimately going to zero when $t \to \infty$. Here the static friction γ is defined as $\gamma=\int_0^\infty dt\,\zeta(t)$, so that

$$\int_0^\infty du\,g(u)=1\ , \tag{2}$$

where $u=t/\tau$. Using hydrodynamic arguments [9] it is possible to show that $\tau=\alpha\gamma$, where α is a constant parametrizing the MFK. The Markovian limit studied by Kramers corresponds to $\zeta(t)=2\gamma\delta(t)$ or $g(u)=2\delta(u)$, where δ is the Dirac delta function.

The Langevin method is equivalent to a Hamiltonian approach [10], where one models the heat bath as a set of independent harmonic oscillators. In the ABC problem, this approach was initiated by Pollak [11] and brought to culmination in the work of PGH [12], where a rate equation valid for all dampings was derived. What is even more important, their work offered the possibility of a systematic attack on the problem for any MFK and for any potential which has a parabolic barrier. Specifically discussed in the PGH paper was exponential friction $g(u)=\exp(-u)$ within the weak-coupling approximation.

It is convenient to discuss the PGH results in the two-dimensional space of variables $1/\alpha^*=1/\alpha\omega_b^2$ and $1/\gamma^*=\omega_b/\gamma$, where ω_b is the usual imaginary barrier frequency. See Fig. 1. The variable $1/\gamma^*$, which is inversely proportional to the static friction, is essentially the time in which the equilibrium Maxwell distribution in velocity is attained in the Markovian limit. The variable $1/\alpha^*$, introduced by van der Zwan and Hynes [5], characterizes the strength of the random force of the medium, called the solvent force. In regions II and III, where α is low and the random forces are strong, the solution to the problem is qualitatively similar to the Kramers case for which α is identically zero. Here energy diffusion is important for low γ^* and spatial diffusion for high γ^*. In regions I and IV, where α^* is high and the random forces are weak, energy diffusion is important

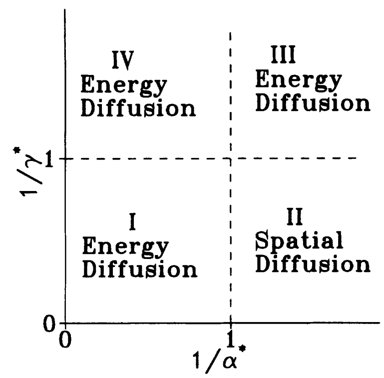

FIG. 1. The various regimes of interest in the two-dimensional space of the variables $1/\alpha^*$ and $1/\gamma^*$.

throughout. Scaling is expected to be valid for large τ which implies that only in region III it is not valid. Now τ can be large in two ways: fixed α, large γ and fixed γ, large α. In this paper, we will only discuss the critical phenomena that occur for large γ. The second case will be discussed in a future publication.

The Hamiltonian of the system is given by [11]

$$H=\frac{p^2}{2M}+V(x)+\sum_{i=1}^{N}\left[\frac{p_i^2}{2m_i}+\frac{1}{2}m_i\left[\omega_i x_i-\frac{c_i x}{m_i\omega_i}\right]^2\right], \tag{3}$$

where the ith bath oscillator has coordinates x_i, momentum p_i, mass m_i, and angular frequency ω_i. The bath oscillators are independent of one another but couple linearly with coefficients c_i to the system coordinate x, of mass M. The coefficients c_i are related to the MFK $\zeta(t)$ by the relation

$$\zeta(t)=\frac{1}{M}\sum_i\left[\frac{c_i^2}{m_i^2\omega_i^2}\cos(\omega_i t)\right]. \tag{4}$$

The potential we choose is given by

$$V(x)=E_b-\tfrac{1}{2}M\omega_b^2x^2,\quad x>-x_0$$
$$V(x)=\infty\ ,\quad x\le -x_0\ . \tag{5}$$

This is an inverted parabola with the barrier top at $x=0$ and a perfectly reflecting wall at $x=-x_0$. We call this the PRW potential. The quantities E_b and x_0 are related by $E_b=\frac{1}{2}M\omega_b^2x_0^2$.

In the next section, we study this model using the GH approach for an exponential memory friction. We will show how the behavior of the rate is described by power laws and how scaling and universality naturally arise in the GH approach.

III. SCALING AND UNIVERSALITY IN THE GH LIMIT FOR EXPONENTIAL FRICTION

When the potential is purely parabolic, we get the GH limit of the ABC problem. Of course, if the barrier height goes to infinity, the rate goes to zero because of the Arrhenius factor. However, if one divides the rate by the transition state theory [1] rate, one gets a finite result in this limit [13]. This is called the reduced rate and it depends only on the MFK. It is given by the largest real and non-negative root of the GH equation [4]

$$r^* = \left[r^* + \frac{\hat{\zeta}(r^*\omega_b)}{\omega_b} \right]^{-1}, \tag{6}$$

where r^* is the reduced rate and $\hat{\zeta}(s)$ is the Laplace transform of the MFK $\zeta(t)$. From (1), we can write

$$\hat{\zeta}(r^*\omega_b) = \gamma \int_0^\infty du\, g(u) \exp(-r^*\alpha^*\gamma^* u) , \tag{7}$$

where the product $r^*\alpha^*\gamma^* u$ can be seen to be equivalent to the Laplace transformation exponent $r^*\omega_b t$. In this section we concentrate on the case of exponential friction where

$$g(u) = g(0)\exp(-k|u|) . \tag{8}$$

In this case, the GH reduced rate is given by

$$r^* = \left[r^* + \frac{g(0)\gamma^*}{k + r^*\alpha^*\gamma^*} \right]^{-1} . \tag{9}$$

For large memory friction time, i.e., when $\tau \gg 1$, three different results are obtained depending on the strength of coupling parameter α. The results are best expressed in terms of the critical coupling $\alpha_c^* \equiv g(0)$ and

$$\Delta = 1 - \alpha_c^*/\alpha^* = 1 - \alpha_c/\alpha , \tag{10}$$

which is proportional to the deviation of α from its critical value. For strong coupling,

$$r^* \approx \frac{k}{\alpha_c^*} \frac{1}{|\Delta|\gamma^*} , \quad \alpha < \alpha_c , \tag{11}$$

but for weak coupling

$$r^* \approx \Delta^{1/2} , \quad \alpha > \alpha_c . \tag{12}$$

When α is close to α_c,

$$r^* \approx \left[\frac{k}{\alpha_c^*} \right]^{1/3} \frac{1}{\gamma^{*1/3}} , \quad \alpha \approx \alpha_c . \tag{13}$$

Exponential friction was previously studied by van der Zwan and Hynes [5]. They in fact studied a more general memory friction which reduced to an exponential one in the extremely overdamped solvent limit. In that case, they obtained the exponents seen in (11)–(13). In addition, PGH [12] also studied this case in detail and found the same exponents. However, the relevance of critical phenomena to these exponents was not appreciated until later [6].

It is clear from looking at these equations that the behavior of the rate for $\gamma^* \gg 1$ changes sharply as one crosses the point $\alpha = \alpha_c$. At the point $\gamma^* = \infty$ and $\alpha = \alpha_c$, the rate is a continuous function of its parameters but its derivative is infinitely discontinuous. Therefore the rate is not an analytical function at the point $\gamma^* = \infty$ and $\alpha = \alpha_c$.

One can see the singularity even more clearly in Fig. 2, where we have plotted the reduced rate as a function of $1/\gamma^*$ for different values of $1/\alpha^*$. For all values of α greater than α_c, the rate has a discontinuous slope at $1/\gamma^* = 0$. As α comes nearer to α_c, the discontinuity remains but decreases in magnitude. At the critical value and below, the discontinuity totally disappears. This is analogous to the behavior of a physical system near a critical point. Consider for example the coexistence of up and down phases in an Ising ferromagnet below its critical point. The spontaneous magnetization disappears when one reaches the Curie point.

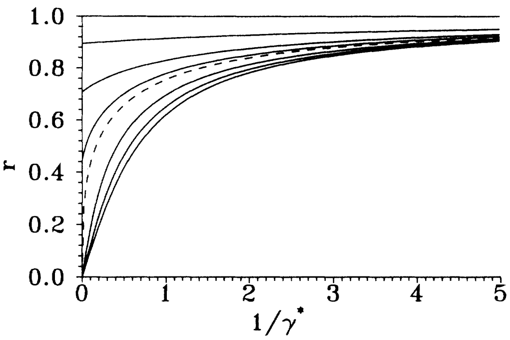

FIG. 2. The plots of the GH reduced rate r^* vs $1/\gamma^*$, the inverse of the memory friction relaxation time, for fixed values of $1/\alpha^*$, the coupling strength, for the case of the simple exponential friction $p = 1$. The values of $1/\alpha^*$ from the top are 0,0.2,0.5,0.8,1 (dashed),2,5,100.

The above analogy can be made even more concrete. Consider the correspondence

$$\begin{aligned} &\text{magnetization} \leftrightarrow r^* , \\ &\text{temperature} \leftrightarrow 1/\alpha^* , \\ &\text{magnetic field} \leftrightarrow 1/\gamma^* . \end{aligned} \tag{14}$$

By using these, one can see that the behavior of the ABC problem in the GH approximation, given in Eqs. (11)–(13), is identical to the mean-field behavior of the Ising model.

We know that, in general, the rate is a function of two parameters α^* and γ^*. Scaling tries to reduce this dependence to one variable by defining scaled parameters. It does not work in the full parameter space, but we know from critical phenomena that it works near a critical point. Scaling also leads to new relations between the exponents, so that the number of independent exponents is reduced. In our case, we see from (11)–(13) that there are four exponents determining the behavior in the critical region, two for Δ and two for γ^*. We will see later that scaling reduces these to just two.

To introduce scaling, let us expand the rate (9) near the critical point $1/\gamma^* = 0$ and $\alpha = \alpha_c$. We get

$$r^{*2} - \Delta - \frac{k}{\alpha_c^* r^* \gamma^*} = 0 . \tag{15}$$

We now introduce scaled variables by the relations

$$f = A r^* \gamma^{*a} , \quad y = B \Delta \gamma^{*b} , \tag{16}$$

where the two exponents a and b and the two amplitudes

A and B are yet to be determined. If scaling is valid, all exponents will be determined in terms of a and b. Introducing these into Eq. (15), one finds

$$f^2 - \frac{A^2 y \gamma^{*2a-b}}{B} - \frac{kA^3\gamma^{*3a-1}}{\alpha_c^* f} = 0 \ . \tag{17}$$

From this, we see that we can make f a function of y alone if we choose

$$a = \tfrac{1}{3}\ , \quad b = 2a = \tfrac{2}{3}\ , \tag{18}$$

independently of the values of A and B. This is expressed by writing

$$r^* = \frac{1}{A\gamma^{*1/3}} f(y)\ , \quad y = B\Delta\gamma^{*2/3}\ , \tag{19}$$

and one says that the rate obeys scaling. The scaling function $f(y)$ is given by

$$f^2 - \frac{A^2 y}{B} - \frac{kA^3}{\alpha_c^* f} = 0\ . \tag{20}$$

Since scaling does not determine A and B, they must cancel out from the behavior of the rate in different regimes. We will see this below.

The scaling behavior is valid in the critical region, i.e., $\alpha \approx \alpha_c$, and $\gamma^* \gg 1$ but for any value of y. Different values of y represent different ways of approaching the critical point. We will now verify that the scaling function has the appropriate behavior in different regimes as seen in Eqs. (11)–(13). In the strong-coupling spatial diffusion regime, α is held fixed at a value less than α_c while γ becomes very large. We see from (16) that in this case y is negative and very large in magnitude. From Eq. (20) we obtain $f(y) \approx (kAB)/(\alpha_c^*|y|)$. Substituting this in Eq. (19), Eq. (11) is reproduced with A and B canceling as expected. In the ABC literature, this is usually called the Smoluchowski limit.

Similarly, in the case of weak coupling, α is held fixed at a value greater than α_c while γ becomes very large. We see from (16) that in this case y is positive and very large. From Eq. (20) we obtain $f(y) \approx A(y/B)^{1/2}$, which when substituted in Eq. (19) reproduces the proper behavior as mentioned in Eq. (12). Of course A and B cancel again. In the chemical literature, this is usually called the solvent caging regime.

Finally, in the intermediate-coupling regime, we have critical coupling, $\alpha = \alpha_c$ and γ becomes very large. We see from Eq. (16) that $y = 0$ and Eq. (20) then gives $f(0) = A(k/\alpha_c^*)^{1/3}$. Substituting this into Eq. (19) we get the rate expression mentioned in Eq. (13), with A and B canceling again. We call this the "core" regime because it lies in the very heart of the critical region.

We can also show scaling pictorially. We take the data in Fig. 2 in the critical region again and replot it by using the scaled rate $f(y)$ and scaled distance from the critical point. The data points all collapse so that we have a function of only one variable. This is shown in Fig. 3. We can also see the asymptotic behaviors of the scaling function for y going to $\pm\infty$.

We saw above that all of the exponents determining the behavior of the rate in the critical region could be expressed in terms of just two, $a = \frac{1}{3}$ and $b = \frac{2}{3}$. The fact that these exponents do not depend on $g(0)$ and k is a manifestation of *exponent* universality of critical phenomena. We will see in Sec. IV that the particular values depend on the fact that the MFK is a simple exponential in nature. For now let us introduce another important concept, the *amplitude* universality.

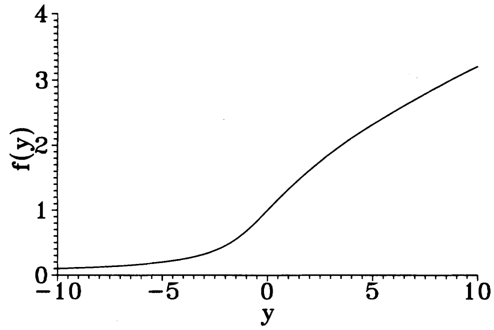

FIG. 3. The plot of the scaled GH rate $f(y)$ vs the scaled deviation from the critical point y for the simple exponential friction case $p = 1$.

Figure 3 shows us that all GH systems with a simple exponential friction but different values of $g(0)$ and k will have a scaling function similar to the one shown in this figure. They will be displaced with respect to each other because of two things. First, the value of $f(y)$ at $y = 0$ depends on k and $g(0)$. Second, the behavior of $f(y)$ for $y \to -\infty$ depends on k and $g(0)$ also. The hypothesis of amplitude universality says that by suitable choice of amplitudes, we can get rid of these dependencies to make even the scaling function universal. The following choice can be seen to satisfy this requirement:

$$A = \left[\frac{\alpha_c^*}{k}\right]^{1/3}\ , \quad B = A^2 = \left[\frac{\alpha_c^*}{k}\right]^{2/3}\ . \tag{21}$$

Equation (20) determining the scaling function $f(y)$ now becomes

$$f^2 - y - \frac{1}{f} = 0\ . \tag{22}$$

This cubic equation can be solved by standard methods. We get

$$f(y) = \left[\frac{4y}{3}\right]^{1/2} \cosh\left[\frac{1}{3}\cosh^{-1}\left[\frac{27}{4y^3}\right]^{1/2}\right]\ , \quad 0 \le y \le (\tfrac{27}{4})^{1/3} \tag{23}$$

$$f(y) = \left[\frac{4y}{3}\right]^{1/2} \cos\left[\frac{1}{3}\cos^{-1}\left[\frac{27}{4y^3}\right]^{1/2}\right]\ , \quad y \ge (\tfrac{27}{4})^{1/3} \tag{24}$$

$$f(y) = \left[\frac{4|y|}{3}\right]^{1/2} \sinh\left[\frac{1}{3}\sinh^{-1}\left[\frac{27}{4|y|^3}\right]^{1/2}\right]\ , \quad y \le 0\ . \tag{25}$$

It can be readily verified that this universal scaling function reproduces the appropriate behavior in different regimes.

In summary, by choosing suitable exponents and amplitudes we have shown that the critical behavior of the rate for a GH system with an exponentially decaying MFK depends only one two exponents and, furthermore, all such systems have the same universal scaling function given by Eqs. (23)–(25). In the critical theory this is expressed by saying that all these systems are in the same universality class. In the next section we generalize these results to determine more universality classes based on the form of the MFK.

IV. SCALING AND UNIVERSALITY FOR GH SYSTEMS WITH GENERAL MFK

In this section we consider the GH theory with more general MFK. It is clear from the discussion of the previous section that the scaling is applicable for large τ, for fixed α, and large γ. Therefore we need to consider the behavior of $g(u)$ in Eq. (1) only for small u. We assume that

$$g(u)\approx g(0)-w|u|^p , \quad u \ll 1 , \tag{26}$$

where w is a positive constant that, for p a positive integer, is related to the pth derivative of $g(u)$ at $u=0$. For all other p values, w is just another amplitude describing the MFK. As examples, we note that for the simple exponential friction studied in the preceding section, $w=kg(0)$ and $p=1$. For the Lee-Robinson friction [14], $\zeta(t)=(2\gamma/\pi t)\sin(t/\alpha\gamma)$, $g(0)=2/\pi$, $w=1/3\pi$, and $p=2$. In fact, one may consider general frictions of the form

$$g(u)=g(0)\exp(-k|u|^p) , \tag{27}$$

in which case $w=kg(0)$. Using Eq. (26) in (7), we find that

$$\hat{\zeta}(r^*\omega_b)=\frac{\omega_b g(0)}{r^*\alpha^*}-\frac{\omega_b w\Gamma(p+1)}{(r^*\alpha^*)^{p+1}\gamma^{*p}} , \tag{28}$$

where $\Gamma(z)$ is the standard gamma function. Substituting Eq. (28) in Eq. (6) and expanding the result for α near α_c, we find

$$r^{*2}-\Delta-\frac{w^*}{r^{*p}\gamma^{*p}}=0 , \tag{29}$$

where

$$w^*=\frac{w\Gamma(p+1)}{\alpha_c^{*p+1}} . \tag{30}$$

Scaling and universality can be discovered exactly as in Sec. III. We omit the details and give the results. It is found that the rate obeys a scaling law of the form

$$r^*=\frac{1}{A_p\gamma^{*p/(p+2)}}f(y) , \quad y=B_p\Delta\gamma^{*2p/(p+2)} , \tag{31}$$

with the amplitudes given by

$$A_p=w^{*-1/(p+2)} , \quad B_p=A_p^2=w^{*-2/(p+2)} . \tag{32}$$

The universal scaling function $f(y)$ is now given by the implicit equation

$$f^2-y-f^{-p}=0 . \tag{33}$$

This equation cannot be solved in general. We have already displayed its solution for the case $p=1$. It can also be solved for the case $p=2$. We get

$$f(y)=\left[\frac{y}{2}+\left[1+\frac{y^2}{4}\right]^{1/2}\right]^{1/2} . \tag{34}$$

In spite of the fact that Eq. (33) cannot be solved in general, the behavior of the rate for general p can be obtained in all of the interesting regimes by studying (33) in various limits and substituting the results in (31). Again we omit the details and give the results. In the spatial diffusion limit, $y\to-\infty$ and we get

$$r^*\approx w^{*1/p}\gamma^{*-1}|\Delta|^{-1/p} , \tag{35}$$

while in the weak-coupling limit, $y\to\infty$ and the rate is given by

$$r^*\approx\Delta^{1/2} . \tag{36}$$

At the critical point $y=0$ and we obtain

$$r^*\approx w^{*1/(p+2)}\gamma^{*-p/(p+2)} . \tag{37}$$

It can be readily seen that all of the results of Sec. III can

TABLE I. Behavior of the rate for the PRW model in the scaling regime for low *scaled* barrier height. The critical value of α is $\alpha_c=g(0)/\omega_b^2$, $\Delta=1-\alpha_c/\alpha$, and $E_b^*=E_b/k_BT$.

Regimes of α	GH	PGH
Strong coupling $\alpha<\alpha_c$	$w^{*1/p}\gamma^{*-1}\|\Delta\|^{-1/p}$	$w^{*1/p}\gamma^{*-1}\|\Delta\|^{-1/p}$
Critical coupling $\alpha=\alpha_c$	$w^{*1/(p+2)}\gamma^{*-p/(p+2)}$	$2p(1+p/2)E_b^*w^{*3/(p+2)}\gamma^{*-3p/(p+2)}$
Weak coupling $\alpha>\alpha_c$	$\Delta^{1/2}$	$2pE_b^*w^*\Delta^{(1-p)/2}\gamma^{*-p}$

be obtained as special cases of the results in this section for $p=1$. A graph of $f(y)$ versus y is shown in Fig. 3 and the results for general p are summarized on the left-hand side of Table I.

In the GH theory, only the parabolic barrier needs to be considered. The other parts of the potential, such as the wall in our case, can be neglected. In this case the reduced rate does not depend on the barrier height. It depends only on the form of the MFK. Remarkably, we have found that in the GH case, the universal scaling function depends only on one parameter of the MFK, namely, p which essentially determines how the friction decays for short times. But in the general problem when the well cannot be neglected, the reduced rate will depend on the barrier height and one will have to introduce a more general scaling form. Guided by our exact results in this section, we introduce a general scaling hypothesis in the next section.

V. GENERAL SCALING HYPOTHESIS

Since the reduced rate depends on the parameters of the MFK and the barrier height E_b, it is reasonable to expect that the scaled rate will involve another scaling combination, the scaled barrier height. Let us assume that the barrier height scales as γ^{*c}. Then we propose that in the scaling region $\alpha \approx \alpha_c$, $\gamma^* \gg 1$ and $E_b^* = E_b/k_BT \gg 1$ [15], the exact reduced rate R^* obeys the scaling hypothesis:

$$R^*(\alpha^*,\gamma^*,E_b^*) \approx \frac{1}{A_p \gamma^{*p/(p+2)}} F(y,z) ,$$
$$y = B_p \Delta\gamma^{*2p/(p+2)} , \tag{38}$$
$$z = C_p E_b^* \gamma^{*-c} .$$

Here the variable y is the scaled distance from the critical point, as before, and the variable z is the scaled barrier height. The exponent c and the amplitude C_p are undetermined at this point as is the dependence of the scaling function $F(y,z)$ on y and z. In writing this hypothesis we have made use of the knowledge we gained in the GH limit which is a special case of (38) for $z \to \infty$. Clearly, $F(y,\infty) = f(y)$. The new exponent c and the new amplitude C_p can depend on both the form of MFK as determined by p and the shape of the well.

We expect that the scaling function $F(y,z)$ will now depend on particular parameter or parameters of the potential which determine its deviation from a pure parabola. As reported in our brief communication [6], we have considered general potentials where the terms of the form x^{2n} are added to the barrier on one side. We have demonstrated that the scaling hypothesis mentioned above is indeed verified and determined the exponents and amplitudes in the PGH formalism. The details of this calculation will be published separately, but we mention some important conclusions here.

As suspected, the new exponent and the new amplitude depend on both the parameters of the MFK and the potential well. The new exponent c is found to be

$$c = 2pn/(p+2)(n-1) . \tag{39}$$

The new amplitude C_p is found to be

$$C_p = w^{*-2n/(p+2)(n-1)} . \tag{40}$$

These results can be summarized by saying that within the PGH approximation, the reduced rate obeys the scaling hypothesis and all systems having potentials determined by the same value of n and having MFK determined by the same value of p belong to the same universality class.

In the next section, we give details of our calculation for the potential (5), i.e., a parabolic barrier joined by a perfectly reflecting wall within the PGH approximation.

VI. SOLUTION OF THE PRW MODEL IN THE PGH APPROXIMATION

The Hamiltonian of the PRW model is given by Eqs. (3) and (5). It is clearly a quadratic form in $N+1$ variables in the barrier region. The nonlinearity which occurs only in the well region is confined to a single point $x=-x_0$. We diagonalize the Hamiltonian with the help of an orthogonal transformation $U=\{u_{ij}\}$, $i,j=0,1,2,\ldots,N$, for all $x>-x_0$ to obtain [11,12]

$$H = \tfrac{1}{2}\dot{\rho}^2 + E_b - \tfrac{1}{2}\lambda_\rho^2\rho^2 + \tfrac{1}{2}\sum_i (\dot{\rho}_i^2 + \lambda_i^2\rho_i^2) , \tag{41}$$

where ρ and ρ_i are the normal mode coordinates in the barrier region and λ_ρ and λ_i are the normal mode frequencies. Henceforth all sums and products will be from 1 to N. The unstable normal mode frequency λ_ρ is equal to $r^*\omega_b$, where r^* is the GH reduced rate introduced previously, which satisfies Eq. (6). The equations of motion for the normal coordinates are given by

$$\ddot{\rho} - \lambda_\rho^2\rho = 0 , \quad \ddot{\rho}_i + \lambda_i^2\rho_i = 0 , \tag{42}$$

in the barrier region, where $x>-x_0$. In this region, all the modes are decoupled from one another and move in a deterministic fashion given by (42).

Because of the presence of the infinite wall in x space, the x coordinate will be reflected at time t_1, say. Since the new unstable mode ρ is related to old unstable mode by $x=(1/\sqrt{M})(u_{00}\rho + \sum_i u_{i0}\rho_i)$, it will receive a "kick" or impulse at this time. This impulse will produce the extra force and the change in energy of the stable bath modes during each round trip of the unstable mode. In the PGH weak-coupling approximation, the zero-order equation of motion for the unstable normal mode does not involve the coupling constant $g_i = u_{i0}/u_{00}$. This amounts to placing the wall in the ρ space at the point $\rho = -\rho^* = -M^{1/2}x_0/u_{00}$.

We start the unstable mode at $t=-\infty$ from the top of the barrier, let it reflect from the wall at $t=0$ and come back to the top of the barrier at $t=\infty$. With these boundary conditions, we can solve for ρ and the extra force. The solution for ρ is given by

$$\rho(t) = -\rho^* \exp(-\lambda_\rho|t|) \tag{43}$$

and the extra force due to the nonlinearity imposed by the wall is given by

$$F(t) = 2\lambda_\rho\rho^*\delta(t) . \tag{44}$$

Once the force is known, the change in the energy of the ρ mode when the system returns to the barrier can be found from Eqs. (3.21) and (3.22) of Ref. [12]. We get

$$E-E'=-\Delta E+\delta E\ , \tag{45}$$

where the average energy loss is

$$\Delta E=2\lambda_\rho^2\rho^{*2}\sum_i g_i^2 \tag{46}$$

and the fluctuation term is

$$\delta E=2\lambda_\rho\rho^*\sum_i g_i\dot{\rho}_i(0)\ . \tag{47}$$

It is easily seen that the fluctuations are Gaussian with zero average and $\langle\delta E^2\rangle=2k_BT\Delta E$, as expected in the PGH approximation. Once the energy loss $\delta=\Delta E/k_BT$ is obtained, the reduced rate is given by [12]

$$R^*=r^*\text{Me}(\delta)\ , \tag{48}$$

where the Mel'nikov-Meshkov integral is given by [16]

$$\text{Me}(u)=\exp\left[\frac{1}{\pi}\int_{-\infty}^{+\infty}dy\frac{\ln[1-e^{-u(1+y^2)/4}]}{1+y^2}\right]\ . \tag{49}$$

The integral cannot be done exactly, but it is easily shown that $\text{Me}(u)\approx 1$ for $u\gg 1$ and $\text{Me}(u)\approx u$ for $u\ll 1$.

We have now obtained the escape rate for the potential (5) for any friction within the PGH approximation. We note that the reduced rate is expressed entirely in terms of the quantities involved in the GH limit. Since we have discussed the GH limit in detail, we will be able to discuss the PGH rate in the scaling region. That is the subject of the next section.

VII. SCALING AND UNIVERSALITY IN THE PGH APPROXIMATION

We see from (48) that the rate is determined by the dimensionless energy loss δ which can be obtained from (46). We get

$$\delta=4\varepsilon(1+\varepsilon)E_b^*r^{*2}\ , \tag{50}$$

where we have used the relations between ρ^* and x_0 and also between λ_ρ and r^*. Here ε is the PGH weak-coupling parameter and is related to u_{00} by the equation: $u_{00}^2=1/(1+\varepsilon)$. It is given by [12]

$$\varepsilon=\sum_i g_i^2=\frac{1}{2r^*\omega_b}\int_0^\infty dt\ \zeta(t)(1-r^*\omega_bt)\exp(-r^*\omega_bt)\ . \tag{51}$$

Using Eq. (1) for $\zeta(t)$, substituting the expansion (26) for $g(u)$ and doing the integral, we obtain

$$\varepsilon=\frac{wp\Gamma(p+1)}{2\alpha^{p+1}\gamma^p(r^*\omega_b)^{p+2}}\ . \tag{52}$$

Expanding this in the scaling region and using information from Sec. IV, we can write ε in the scaled form

$$\varepsilon=\frac{p}{2f(y)^{p+2}}\ . \tag{53}$$

Substituting this in (50) and using the scaling form (31) for r^*, we get

$$\delta=\frac{2p}{f^p}\left[1+\frac{p}{2f^{p+2}}\right]\frac{E_b^*}{A_p^2\gamma^{*2p/(p+2)}}\ . \tag{54}$$

From this equation we see clearly that the barrier height scales with a new exponent and there is also a new amplitude. By comparison with Eq. (38), we conclude that the hypothesis is satisfied with

$$c=2p/(p+2) \tag{55}$$

and

$$C_p=1/A_p^2\ . \tag{56}$$

The scaling function is given by

$$F(y,z)=f(y)\text{Me}[\delta(y,z)]\ , \tag{57}$$

where the energy loss is given by

$$\delta(y,z)=\frac{2p}{f(y)^p}\left[1+\frac{p}{2f(y)^{p+2}}\right]z\ . \tag{58}$$

Having shown that the reduced rate in the PGH approximation obeys scaling and universality proposed by us in Eq. (38), we can now study its behavior in different scaling regimes. It should be kept in mind that all of the following statements are made in the scaling region and they may or may not be applicable beyond this region. First of all it is clear that when $z\gg 1$, the energy loss becomes very large making $\text{Me}(\delta)\approx 1$. Two variable scaling function $F(y,z)$ reduces to the one variable scaling function $f(y)$ encountered in the GH case. Therefore, at least in the scaling region, one does not have to let the barrier height E_b go to infinity to see the GH results: the condition $E_b^*\gg\gamma^{*2p/(p+2)}$ is sufficient. Of course once the GH rate is obtained one may get all the relevant limiting cases (11)–(13) as before.

For a finite but fixed z, we have three cases to consider depending on the coupling strength as usual. In the strong-coupling case, $y\to-\infty$, and, from Eq. (33), we find that $f(y)$ goes to 0 as $1/|y|^p$. From (58) we see that the energy loss is very large. Therefore, in this case the GH behavior is obtained for any fixed z. In the weak-coupling case, y is positive and very large. From (33), we can find that $f(y)$ goes to infinity like $y^{1/2}$. From (58), we find that the energy loss is very small for a fixed z, so that we can use the fact that $\text{Me}(\delta)\approx\delta$. This means that $F(y,z)\approx 2py^{(1-p)/2}z$. Therefore, the GH limit is obtained, if $p<1$. If $p\geq 1$, the GH limit is never obtained. The ultimate behavior of the rate for large y is given by

$$R^*\approx 2pE_b^*w^*\Delta^{(1-p)/2}\gamma^{*-p}\ . \tag{59}$$

Finally, in the core regime, $y\approx 0$ and from (33) we obtain that $f(y)\approx 1$. Therefore from (58), the energy loss is proportional to z. For large fixed z, we will see the GH behavior. For small fixed z, we will see deviations from this behavior. In this case, the rate is easily seen to be given by

$$R^*\approx 2p(1+p/2)E_b^*w^{*3/(p+2)}\gamma^{*-3p/(p+2)}\ . \tag{60}$$

In the next section, we discuss the piecewise parabolic potential model studied by PGH from the scaling point of view and show that this model and the PRW model are in the same universality class.

VIII. THE PIECEWISE PARABOLIC POTENTIAL CASE

In order to discuss the results of PGH [12] in the scaling limit, we have to know the behavior of many quantities appearing in their energy-loss expression (4.25). We already know that the GH frequency goes to zero. From their Eqs. (4.22) and (4.23), we see that their quantities ζ and σ also go to zero in the scaling limit. On the other hand, the renormalized well frequency λ_0 and the well crossing time t_p tend to finite limits. From Eqs. (4.15) and (4.20), we deduce that

$$\lambda_0^2 = u_{00}^2(\omega_0^2+\omega_b^2)\ , \quad t_p=\pi/\lambda_0\ . \tag{61}$$

Substituting all this in Eq. (4.25), we see that the value $R(0)$ of the integral (4.26) is needed. This is obtained either directly from (4.26) or from (4.27). We get

$$R(0)=2/\lambda_p^2\ . \tag{62}$$

All this information gives the average energy loss in the scaling limit. We obtain

$$\Delta E = 4\varepsilon(1+\varepsilon)E_b r^{*2}\omega_0^2/(\omega_0^2+\omega_b^2)\ . \tag{63}$$

Comparing this with the energy loss in the PRW model given by our Eq. (50), we see that the two are identical except for the factor $\omega_0^2/(\omega_0^2+\omega_b^2)$ in the potential studied by PGH. Clearly the behavior of the two models is identical and they belong to the same universality class. The only difference is that the amplitude C_p in their model is given by

$$C_p=(1/A_p^2)[\omega_0^2/(\omega_0^2+\omega_b^2)]\ . \tag{64}$$

From the set of exponents and scaling functions that we have obtained, we can draw the following conclusion. All PRW and piecewise parabolic potential models with the same values of p are in the same universality class. They may have different critical strengths and their other amplitudes may be different, but they have identical set of exponents and scaling functions.

IX. CONCLUDING REMARKS

In summary, we have proposed a scaling hypothesis to describe the behavior of the escape rate in the ABC problem. We have verified that the hypothesis is valid for the purely parabolic GH model for a general class of frictions. We found that all the GH models fall into universality classes based on a single parameter p of the MFK. This parameter governs the short-time behavior of the MFK. We have also verified that the hypothesis is applicable to the PRW model within the PGH weak-coupling approximation. In this case one needs an additional exponent and amplitude to scale the barrier height. We find that the PRW and the piecewise parabolic models considered by PGH fall into the same universality class. As mentioned before we have already verified the hypothesis for a general class of potentials in the PGH approximation. We have also proposed and verified another hypothesis valid for the case of large α and fixed γ. All of these will be published in the future [17].

Having obtained the information in the critical region (except perhaps in the "core"), it should be possible to obtain accurate estimates of the exact rate by using standard methods of critical theory [8]. One may derive the exact high and low α series expansions for the rate and then use Domb's method or the Padé approximant method to extrapolate to the exact result accurately. One advantage of the procedure is that the critical "temperature" α_c is known exactly. This will enable one to get good results for exponents and scaling functions. Also, one might be able to use the information in the critical region in conjunction with series expansions to obtain the rate in the whole parameter space. It would be tremendously interesting to study the ABC problem from the renormalization-group [18] point of view. This is another scheme, which, apart from explaining critical phenomena, has been instrumental in yielding information about the problem far away from the critical region.

Finally, we would like to remark on the possibility of verifying the scaling hypothesis experimentally. Usually, the experiments are very difficult to interpret theoretically because the models are, at best, caricatures of physical reality. They neglect many things and emphasize others. But the hypothesis of universality will help us here. According to this hypothesis, the universal quantities such as the exponents and scaling functions depend on very few crucial parameters of the system. As mentioned before, even in the GH model, the universal features depend on just one parameter p. All others, such as $g(0)$ and k, are totally irrelevant. Therefore, many experimental systems will have similar behavior. In the field of critical phenomena, we know already that liquids, liquid mixtures, binary alloys, and uniaxial ferromagnets are in the same universality class as the nearest-neighbor Ising model. All of these physical systems have complicated many-body interactions having different origins, but they all behave identically in the critical region. The only differences are in the nonuniversal quantities such as the amplitudes. But even with these differences, the amplitude universality can be used to make the scaling functions universal.

In closing, we hope that this "union" of two seemingly different phenomena will prove valuable in future theoretical studies of the ABC problem. Researchers in the field of critical phenomena should be able to bring to bear their specialized methods to obtain further studies of the ABC problem.

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