Space-dependent friction in the theory of activated rate processes

R. Krishnan, Surjit Singh, and G. W. Robinson
SubPicosecond and Quantum Radiation Laboratory, Departments of Physics and Chemistry, P.O. Box 41061, Texas Tech University, Lubbock, Texas 79409-1061
(Received 12 November 1991)

The Carmeli-Nitzan approach to the theory of activated rate processes is generalized to allow for different frictions in the well and barrier regions. Many previous results are recovered as special cases and some new results are obtained and discussed.

PACS number(s): 05.40.+j, 82.20.Db

I. INTRODUCTION

The problem of thermally activated barrier crossing is important in many areas of physics and chemistry [1]. A customary approach to this problem, pioneered by Kramers [2], starts with a Langevin equation where the effects of the bath are introduced by including a damping friction force and a random force. Kramers's theory has been generalized in many directions. For example, the assumption of Markovian friction used by Kramers was relaxed by Grote and Hynes [3], both in the low- and the high-damping regimes. In the low-damping regime, the generalization to a frequency-dependent friction was also achieved independently by Carmeli and Nitzan [4]. In addition to this, various approximate equations have been proposed to provide a unified expression for the escape rate for all dampings [5,6]. More recently, Pollak, Grabert, and Hänggi [7] used the Hamiltonian approach [8] to solve the problem for the whole range of damping without the use of *ad hoc* adjustments.

In the meantime, from various studies [9–11], it has been realized that the friction kernel must be a function of the spatial coordinate also. In particular, friction kernels near the well and the barrier can be quite different from each other. Even though the escape problem with a general space-dependent friction cannot be solved, many attempts have been made to solve the problem for low and high damping separately [12].

Recently, using both the Langevin equation and the Hamiltonian approach, we have found analytical solutions to the barrier-crossing problem where the well and the barrier regimes have different space-independent frictions. Preliminary results from the first approach have already been published [13]. In the present paper, we provide more details about this calculation, which is based on the Carmeli-Nitzan method. The results for the approach based on the Hamiltonian will be published elsewhere [14].

In Sec. II we introduce our model and derive an expression for the rate. In Sec. III we deal with the energy-dependent diffusion coefficient which is needed for the evaluation of the escape rate. In Sec. IV we present and discuss our results for the escape rate in different cases. We offer our concluding remarks in Sec. V.

II. MODEL AND SOLUTION

We start with a particle of mass M moving in a one-dimensional piecewise harmonic potential $V(x)$ (see Fig. 1) given by

$$V(x)=\begin{cases}\frac{1}{2}M\omega_0^2x^2\ , & x<x_0\\ E_b-\frac{1}{2}M\omega_b^2(x-x_b)^2\ , & x>x_0\ ,\end{cases} \tag{1}$$

where ω_0 is the well frequency, E_b is the barrier height, ω_b is the frequency parameter determining the barrier shape, and x_b gives the location of the barrier top. The conditions of the continuity of the potential and force at the seam x_0 give

$$x_b=x_0(1+\mu^{-2})\ ,\quad E_b=\tfrac{1}{2}M\omega_0^2x_0^2(1+\mu^{-2})\ , \tag{2}$$

where $\mu=\omega_b/\omega_0$. In the well region, the motion of the particle is assumed to be governed by the generalized Langevin equation,

$$\frac{dv}{dt}=-\frac{1}{M}\frac{dV(x)}{dx}-\int_0^t dt'\zeta_w(t-t')v(t')+\frac{1}{M}R_w(t)\ , \tag{3}$$

where v is the velocity of the particle, $\zeta_w(t)$ is the memory friction kernel (MFK) in the well region, and $R_w(t)$ is the usual random force satisfying the conditions

$$\langle R_w(t)\rangle=0\ ,\quad \langle R_w(t)R_w(0)\rangle=Mk_BT\zeta_w(t)\ . \tag{4}$$

Here k_B is the Boltzmann constant and T is the temperature of the heat bath. Similar equations are assumed to apply in the barrier region with the subscript w replaced by b. Assuming that only one relaxation time is important in each region, we can see from dimensional arguments that the MFK's must have the form

$$\zeta_i(t)=(\gamma_i/\tau_i)g_i(t/\tau_i)\ ,\quad i=w,b\ , \tag{5}$$

where the γ_i's are the damping rates, the τ_i's are the relaxation times, and the g_i's are dimensionless functions of their dimensionless arguments.

Now we solve the Langevin equations in the two regions separately and join the solutions by a procedure

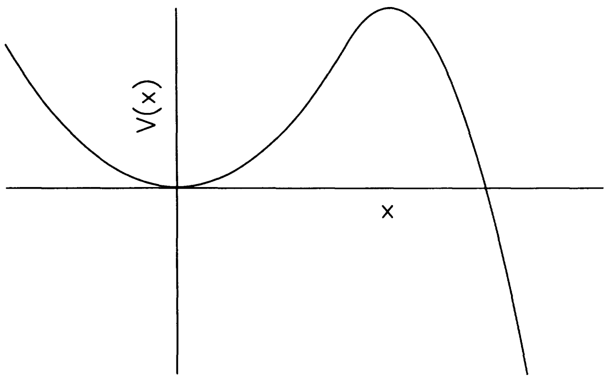

FIG. 1. A schematic picture of the piecewise parabolic potential given by Eq. (1).

that exactly parallels the one used by Carmeli and Nitzan [5]. The result for the escape rate is

$$r=(t_w+S/r_{\mathrm{GH}})^{-1} , \tag{6}$$

where r_{GH} is the Grote-Hynes [3] rate,

$$r_{\mathrm{GH}}=\frac{\lambda_0}{2\pi\mu}\exp(-E_b/k_BT) , \tag{7}$$

with λ_0 being the largest (real and positive) root of the equation

$$\lambda^2-\omega_b^2+\lambda\hat{\zeta}_b(\lambda)=0 , \tag{8}$$

with

$$\hat{\zeta}_b(\lambda)=\int_0^\infty dt\,\exp(-t\lambda)\zeta_b(t) . \tag{9}$$

The other quantities in Eq. (6) are as follows. The quantity t_w is the mean first passage time to reach the matching energy E_1 and is given by

$$t_w=\frac{1}{k_BT}\int_0^{J_1}\frac{dJ}{\varepsilon_w(J)}\exp(E/k_BT)\int_0^J dJ'\exp(-E'/k_BT) . \tag{10}$$

Here $\varepsilon_w(J)$ is given by [3,4]

$$\varepsilon_w(J)=\frac{M}{\omega^2}\int_0^\infty dt\,\zeta_w(t)\langle v(0)v(t)\rangle , \tag{11}$$

where $\langle v(0)v(t)\rangle$ is the velocity-velocity autocorrelation function of the system with no friction, ω is the angular frequency of the motion, and J is the action,

$$J=\frac{M}{2\pi}\oint dx\,v(x) , \tag{12}$$

where the integral is taken over a full period of motion. It should be noted that $\varepsilon_w(J)$ is related to the energy-diffusion constant by the relation

$$D(E)=k_BT\varepsilon_w(J) . \tag{13}$$

The matching energy E_1 satisfies the equation

$$\exp[-\alpha_b(E_b-E_1)/k_BT]=\frac{[\alpha_bk_BT(E_b-E_1)]^{1/2}}{\varepsilon_w(J_1)\omega(J_1)(\alpha_b+1)\sqrt{\pi}} , \tag{14}$$

where α_b is given by

$$\alpha_b=\lambda_0^2/(\omega_b^2-\lambda_0^2) . \tag{15}$$

The factor S in Eq. (6) is what distinguishes the Carmeli-Nitzan result from other simpler connection formulas. This factor ensures that the number of particles is conserved throughout and that the probability distribution is continuous at the matching point. This factor is given by

$$S=\frac{\omega_0}{k_BT}\int_0^{E_b}\frac{dE}{\omega}\exp(-E/k_BT)\times\left[\left[\frac{1+R}{2}\right]\eta(E_1-E)+\eta(E-E_1)\right] , \tag{16}$$

where $\eta(E)=0$ for $E<0$, $\eta(E)=1$ for $E>0$, and

$$R=\operatorname{erf}\{[(\alpha_b+1)(E_b-E_1)/k_BT]^{1/2}\} , \tag{17}$$

with erf(x) being the standard error function.

Now, let us discuss the rate expression (6) in some special limits. First of all, if $\zeta_w(t)=\zeta_b(t)$, we get the Carmeli-Nitzan result, as expected. Next, if we assume that $\gamma_w\to\infty$, implying instantaneous equilibrium in the well region, we obtain $t_w\to 0$, $S\to 1$, so that $r\to r_{\mathrm{GH}}$. This is also expected because the Grote-Hynes result specifically assumes equilibrium in the well. If, further, we assume that the barrier friction is static, i.e., $\zeta_b(t)=2\gamma_b\delta(t)$, we get the Kramers intermediate- to high-friction result, as expected. On the other hand, if we assume $\gamma_b\to 0$ with $\gamma_w\to\infty$, we get the transition-state theory (TST) result. This implies that TST assumes equilibrium in the *well* and no recrossing at the *barrier*. It is clear that if friction is space independent, as is the case with usual treatments, one could not satisfy the two postulates ($\gamma\to\infty$ and $\gamma\to 0$) simultaneously. However, there would be no mathematical contradiction if the well and the barrier regions can have different frictions, as is the case in this paper.

III. ENERGY-DIFFUSION CONSTANT

In this section, we calculate $\varepsilon_w(J)$. This quantity, which is directly related to the energy-diffusion constant, is given by Eq. (11). The inner integral $\langle v(0)v(t)\rangle$ in that equation depends on the shape of the potential; and the outer one on the form of the friction. This relation can be transformed further by introducing the Fourier components of the velocity,

$$v(t)=\sum_{n=-\infty}^{\infty}C_n\exp(in\omega t) , \tag{18}$$

$$C_n=\frac{\omega}{2\pi}\int_0^{2\pi/\omega}dt\,v(t)\exp(-in\omega t) . \tag{19}$$

We then obtain

$$\varepsilon_w(J)=\frac{M}{2\omega^2}\sum_{n=-\infty}^{\infty}|C_n|^2\zeta_w^n(t)\ , \tag{20}$$

with

$$\zeta_w^n(t)=\int_{-\infty}^{\infty}dt\ \zeta_w(t)\cos(n\omega t)\ . \tag{21}$$

Written in this form, the dependence of $\varepsilon_w(J)$ on the potential and on the MFK is seen to be separated even further.

To proceed, we need to choose a specific form for $\zeta_w(t)$. Two have been used. The first one is the usual exponential MFK,

$$\zeta_w^{\text{ex}}(t)=\frac{\gamma_w}{\tau_w}\exp(-|t|/\tau_w)\ . \tag{22}$$

The second is a variant of Lee-Robinson (LR) friction form [15], which has proven to be very useful in fitting both experimental and molecular dynamics simulation data [16–18]:

$$\zeta_w^{\text{LR}}(t)=\frac{2\gamma_w}{\pi t}[\sin(t/\tau_w)+\sin(100t/\tau_w)]\ . \tag{23}$$

From (22) and (23), we can calculate $\zeta_w^n(t)$ by using (21) and doing simple integrals. For the Lee-Robinson friction,

$$\varepsilon_w^{\text{LR}}(J)=\frac{M\gamma_w}{\omega^2}\sum_{n=-\infty}^{\infty}|C_n|^2 f_n\ , \tag{24}$$

with the following values for f_n:

$$f_n=\begin{cases}2\ , & |n|<\dfrac{1}{\omega\tau_w}\\ 1\frac{1}{2}\ , & |n|=\dfrac{1}{\omega\tau_w}\\ 1\ , & \dfrac{1}{\omega\tau_w}<|n|<\dfrac{100}{\omega\tau_w}\\ \frac{1}{2}\ , & |n|=\dfrac{100}{\omega\tau_w}\\ 0\ , & |n|>\dfrac{100}{\omega\tau_w}\ .\end{cases} \tag{25}$$

For the exponential friction, we obtain

$$\varepsilon_w^{\text{ex}}(J)=\frac{M\gamma_w}{\omega^2}\sum_{n=-\infty}^{\infty}\frac{|C_n|^2}{(1+n^2\omega^2\tau_w^2)}\ , \tag{26}$$

where the C_n's in Eqs. (24) and (26) are given by Eq. (19).

The next step is to calculate these C_n's which depend on the friction-free motion of the particle in the given potential. The available range of energies between 0 nd E_b divides naturally into two sections at $x=x_0$ and $E=E_0=E_b\mu^2/(1+\mu^2)$. For $E<E_0$, we have a simple harmonic oscillator with frequency ω_0. We start the particle at the turning point $x_1=-(2E/M\omega_0^2)^{1/2}$ with $v=0$ and get

$$v(t)=\left[\frac{2E}{M}\right]^{1/2}\sin\omega_0 t\ , \tag{27}$$

for all t. For $E>E_0$, we again start the particle from x_1 at $t=0$, let it reach the seam $x=x_0$ at $t=t^*$ and the other turning point $x_2=x_b-[2(E_b-E)/M\omega_b^2]^{1/2}$ at $t=\pi/\omega$. The velocity is given by

$$v(t)=\begin{cases}-\omega_0 x_1\sin(\omega_0 t)\ , & 0\le t\le t^*\\ \omega_b(x_b-x_2)\sinh\left[\omega_b\left[\dfrac{\pi}{\omega}-t\right]\right]\ , & t^*\le t\le\dfrac{\pi}{\omega}\ .\end{cases} \tag{28}$$

Here the time t^* is given by

$$\sin(\omega_0 t^*)=(1-E_0/E)^{1/2}\ ,\quad \cos(\omega_0 t^*)=-(E_0/E)^{1/2}\ . \tag{29}$$

From these expressions for the velocity, we can then calculate $J(E)$ using (12) and C_n using (19). For $E<E_0$,

$$J(E)=E/\omega_0\ ,\qquad C_n=-i\left[\frac{E}{2M}\right]^{1/2}(\delta_{n,1}-\delta_{n,-1})\ , \tag{30}$$

where $\delta_{i,j}$ is the Kronecker delta. For $E>E_0$,

$$J(E)=\frac{Et^*}{\pi}-\frac{E}{\pi\omega_0}\sin(\omega_0 t^*)\cos(\omega_0 t^*)+\frac{(E_b-E)}{\pi\omega_b}(\sinh\theta\cosh\theta-\theta)\ ,\qquad \theta=\omega_b\left[\frac{\pi}{\omega}-t^*\right]\ , \tag{31}$$

and

$$C_n=\left[\frac{i\omega\omega_0 x_1}{2\pi}\right]\left[\frac{\sin(\omega_0 t^*-n\omega t^*)}{\omega_0-n\omega}-\frac{\sin(\omega_0 t^*+n\omega t^*)}{\omega_0+n\omega}\right]-\frac{i\omega\omega_b}{\pi}(x_b-x_2)\left[\frac{n\omega\cos(n\omega t^*)\sinh\theta+\omega_b\sin(n\omega t^*)\cosh\theta}{\omega_b^2+n^2\omega^2}\right]\ . \tag{32}$$

Now we can substitute these C_n's into (24) and (26) to get $\varepsilon_w(J)$. If $E<E_0$, only the terms $n=\pm 1$ contribute, and the resulting expressions are simple. For $E>E_0$, one has to evaluate the whole sum. For the LR friction, the sum involved is finite, since $f_n=0$ for sufficiently high n [see Eqs. (25)], so we can calculate it term by term. In the case of the exponential friction, the sum can be found analytically. The calculation is straightforward but lengthy and is outlined in the Appendix. In both cases, for the purpose of calculation of our final rate expressions, we evaluate the analytical expressions on a computer.

IV. CALCULATIONS AND DISCUSSION

We choose the potential such that $\mu=2$, $E_b/k_BT=10$. No other parameters for the potential are needed. We choose different ratios of $\lambda=\gamma_b/\gamma_w$, typically from 0.01 to 100, and values of $\omega_0\tau_w$ and $\omega_0\tau_b$ from 1 to 100. We determine the rate on a logarithmic scale for γ_b/ω_0 from 10^{-4} to 10^4. The procedure used is as follows. For a given γ_b/ω_0, we first solve the Grote-Hynes equation (8) for λ_0 and then solve Eq. (14) for the matching energy E_1/E_b. Then the integral S and the double integral for t_w in (10) are evaluated. Wherever needed, $\varepsilon_w(J)$ from (24)–(26) for the appropriate friction was used. The rate could then be calculated using Eq. (6). The reduced rate, i.e., the actual rate normalized by the TST rate, was plotted against γ_b/ω_0 for the different cases.

Since the results for the LR case have been presented and discussed earlier [13], here we will focus on the results from the exponential case. Also, since the static limit is the same for both friction functions, we will not discuss it here. The reader is referred to Fig. 2 of Ref. [13] for this limit.

In Fig. 2 of the current paper, we vary $\lambda=\gamma_w/\gamma_b$ in the exponential friction case with $\omega_0\tau_w=\omega_0\tau_b=10$. The results of this variation clearly show that the higher the value of λ, the nearer the rate is to the Grote-Hynes result over the full range of friction. For very high λ, the Grote-Hynes result is valid everywhere except for extremely low γ_b or γ_w. This is because the region in the vicinity of the well is no longer in equilibrium as required by the Grote-Hynes rate expression (7). Therefore one always sees for sufficiently large λ a middle region along the γ_b/ω_0 axis where TST is valid. On the other hand, for very low λ, the well region remains out of equilibrium even for moderate γ_b because γ_w is too small. In this case TST is never valid. The dividing line between the two behaviors is when λ is of order unity.

In Fig. 3, λ and τ_b are kept fixed while τ_w is varied. Again the high-γ_b region is unaffected. In the low-γ_b region, the dynamics in the vicinity of the well dominates the rate, which is seen to increase with decreasing τ_w because that causes the well friction to decrease. Of course,

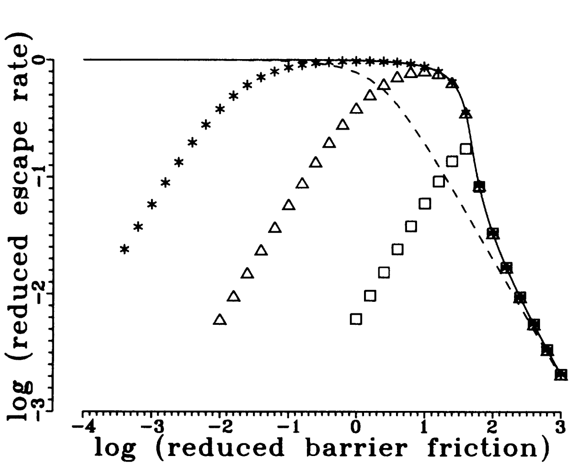

FIG. 2. The logarithm of the reduced escape rate R^* normalized to the TST rate vs the logarithm of the reduced barrier friction γ_b/ω_0 for the case of exponential friction for different values of $\lambda=\gamma_w/\gamma_b$ for $\omega_0\tau_w=\omega_0\tau_b=10$. The stars, triangles, and squares correspond to $\lambda=100$, 1, and 0.01, respectively. The dashed line is the Kramers result and the solid line is the GH result.

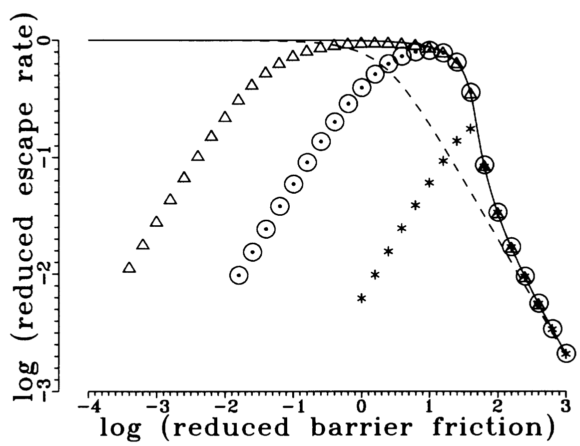

FIG. 3. Same as Fig. 2 but for $\lambda=1$, $\omega_0\tau_b=10$, and $\omega_0\tau_w=100$, 10, and 1 for the stars, circles, and triangles, respectively.

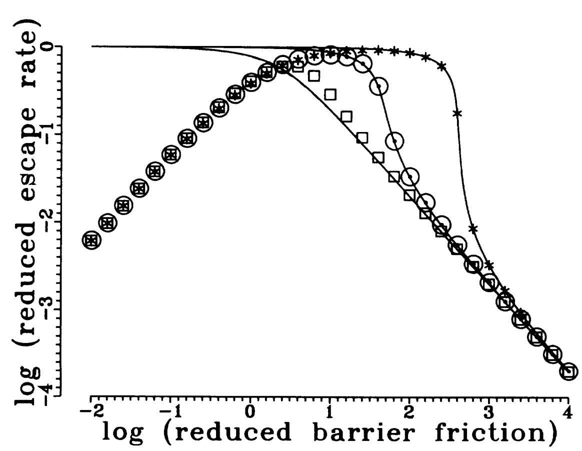

FIG. 4. Same as Fig. 2 but for $\lambda=1$, $\omega_0\tau_w=10$, and $\omega_0\tau_b=100$, 10, and 0.01 for the stars, circles, and squares, respectively. In this case, the Kramers result is indistinguishable from the GH result for the case $\omega_0\tau_b=0.01$.

the limiting rate is provided by the static limit $\tau_w=0$. To increase the rate further in this region one would have to increase λ.

In Fig. 4, we vary τ_b. Here, the low-γ_b results are not affected because the well dynamics are not changed. The high-γ_b rates approach the appropriate Grote-Hynes result for each τ_b. The low-τ_b results are closest to the Kramers result, as expected. The high-τ_b results have a region where TST is applicable. The width of this region increases for increasing τ_b since this decreases the friction in the barrier region.

V. CONCLUDING REMARKS

In conclusion, we have plotted and discussed in a variety of cases the escape rate for a particle from a well where there is space-dependent non-Markovian exponential friction. We have used the Langevin equation approach augmented by the Carmeli-Nitzan scheme for obtaining a unified rate expression. We have done the calculations for two forms of dynamic friction: the exponential and the Lee-Robinson form. The latter is equivalent to a Gaussian friction in its short-time behavior. The results from the LR friction were reported earlier [13] and the results from the exponential friction are discussed here. In comparing the two sets of results, we find the following. In the high-friction regime, the two sets of results are not much different. However, in the low-friction regime the results are dramatically different. In particular, compare Fig. 4 in Ref. [13] with Fig. 3 here. In the LR case, the rate depends on τ_w very weakly and in the exponential case it varies as τ_w^{-2} for $\gamma_b \ll \omega_0$. In the low-friction case, the well dynamics plays a dominant role and the rate is determined by t_w [see Eq. (6)], which itself is determined by $\varepsilon_w(J)$, see Eq. (10). For the LR case, we see from Eqs. (24) and (25) that the dependence on τ_w is not very strong: f_n ranges between $\frac{1}{2}$ and 2. In the exponential case, however, the dependence of $\varepsilon_w(J)$ on τ_w can be dramatic. For instance, on examining Eq. (26), when the well dominates, ω is very small and the 1 in the denominator can be neglected, giving rise to $\varepsilon_w(J)\propto\tau_w^{-2}$. This then explains the differences between the two friction cases. In this connection, it should be noted that a similar explanation of the strong dependence of the rate on the relaxation time for low damping was given by Fonseca *et al.* [19] in terms of Grigolini's decoupling effect [20].

A recent approach by Pollak, Grabert, and Hänggi (PGH) [7] based on the Hamiltonian model derives these rate expressions in a theoretically more fundamental way. This method represents a system particle in a heat bath, not within the confines of a Langevin equation, but rather as a collection of coupled oscillators. It would therefore be most interesting to compare the results obtained in the present paper with those from PGH theory. In fact, we have recently generalized the PGH method to the case of space-dependent friction. As would be expected, there are strong qualitative similarities between the two sets of results, as well as some clear differences. These results will be reported elsewhere [14].

ACKNOWLEDGMENTS

Financial support at the SPQR Laboratory has been shared by the Robert A. Welch Foundation (Grant Nos. D-0005 and D-1094), the National Science Foundation (Grant No. CHE-9112002), and the State of Texas Advanced Research Program (Grant No. 003644-004).

APPENDIX

In this Appendix, we give details of the calculation of $\varepsilon_w^{ex}(J)$. First of all, we rewrite Eq. (26) as

$$\varepsilon_w^{ex}(J)=\frac{M\gamma_w}{\omega^2\tau_w^2}\sum_{n=-\infty}^{\infty}\frac{|C_n|^2}{(\tau_w^{-2}+n^2\omega^2)} . \tag{A1}$$

For $E<E_0$, in which case $\omega=\omega_0$ and the C_n are given by (30). Only the terms $n=\pm 1$ contribute and we get

$$\varepsilon_w^{ex}(J)=\frac{E\gamma_w}{\omega_0^2(1+\omega_0^2\tau_w^2)} .$$

For $E>E_0$, the C_n are given by Eq. (32). Before proceeding further we rewrite C_n as

$$C_n=i[C^{(1)}\sin(n\omega t^*)+nC^{(2)}\cos(n\omega t^*)]\times\left[\frac{1}{\omega_0^2-n^2\omega^2}+\frac{1}{\omega_b^2+n^2\omega^2}\right] \tag{A2}$$

with

$$C^{(1)}=-\frac{\omega\omega_0}{\pi}\left[\frac{2E_0}{M}\right]^{1/2} , \tag{A3}$$

$$C^{(2)}=-\frac{\omega^2}{\pi}\left[\frac{2(E-E_0)}{M}\right]^{1/2} . \tag{A4}$$

In obtaining these, we have used the requirement that velocity is continuous at t^*, which, using Eqs. (28) and (29), is equivalent to

$$\begin{aligned}\sinh\theta&=[(E-E_0)/(E_b-E)]^{1/2} ,\\ \cosh\theta&=[(E_b-E_0)/(E_b-E)]^{1/2} .\end{aligned} \tag{A5}$$

After substituting (A2) in (A1) and expanding, we see that we have to evaluate nine types of infinite sums. The numerators in the general terms in these sums are $\sin^2(n\omega t^*)$, $n^2\cos^2(n\omega t^*)$, $2n\sin(n\omega t^*)\cos(n\omega t^*)$, and the denominators are

$$(\omega_0^2-n^2\omega^2)^2(\tau_w^{-2}+n^2\omega^2),\quad(\omega_b^2+n^2\omega^2)^2(\tau_w^{-2}+n^2\omega^2) ,$$
$$(\omega_0^2-n^2\omega^2)(\omega_b^2+n^2\omega^2)(\tau_w^{-2}+n^2\omega^2) .$$

The first step in doing sums like these is to reduce the number of factors from three to two in the denominator. This is accomplished by using identities such as

$$\frac{1}{(a-x)^2(b+x)}=\frac{1}{(a+b)}\left[\frac{1}{(a-x)^2}+\frac{1}{(a-x)(b+x)}\right] , \tag{A6}$$

$$\frac{1}{(a-x)(c+x)(b+x)}=\frac{1}{(c+a)}\left[\frac{1}{(a-x)(b+x)}+\frac{1}{(c+x)(b+x)}\right]. \tag{A7}$$

This causes the denominators to be of the type $(\omega_0^2-n^2\omega^2)^2$, $(\omega_b^2+n^2\omega^2)^2$, $(\omega_0^2-n^2\omega^2)(\tau_w^{-2}+n^2\omega^2)$, and $(\omega_b^2+n^2\omega^2)(\tau_w^{-2}+n^2\omega^2)$. The second step is to discover relationships within these sums. We note that the second and the fourth types of denominators can be obtained from the first and the third types, respectively, by changing ω_0^2 to $-\omega_b^2$. This leaves us with denominators of the type $(\omega_0^2-n^2\omega^2)^2$ and $(\omega_0^2-n^2\omega^2)(\tau_w^{-2}+n^2\omega^2)$ only.

Now we turn our attention to the numerators. The numerator $2n\sin(n\omega t^*)\cos(n\omega t^*)$ can be obtained by differentiating the numerator $\sin^2(n\omega t^*)$ with respect to t^*. This leaves us with numerators of the type $\sin^2(n\omega t^*)$ and $n^2\cos^2(n\omega t^*)$. Both of these can be obtained from a numerator of the type $\cos(2n\omega t^*)$. To obtain $\sin^2(n\omega t^*)$, we use the fact that $\sin^2(n\omega t^*)=\frac{1}{2}[1-\cos(2n\omega t^*)]$ and the result with 1 in the numerator may be obtained by taking the limit $t^*\to 0$ in the result with $\cos(2n\omega t^*)$ in the numerator. To obtain a sum with a numerator $n^2\cos^2(n\omega t^*)$, we use the following two steps. First we differentiate the result for $\cos(2n\omega t^*)$ twice with respect to t^* to get the result for $n^2\cos(2n\omega t^*)$ and then we use the identity $\cos^2(n\omega t^*)=\frac{1}{2}[1+\cos(2n\omega t^*)]$.

In the final analysis, we have to evaluate only the sums

$$S_1=\sum_{n=-\infty}^{\infty}\frac{\cos(2n\omega t^*)}{(\omega_0^2-n^2\omega^2)^2}, \tag{A8}$$

$$S_2=\sum_{n=-\infty}^{\infty}\frac{\cos(2n\omega t^*)}{(\omega_0^2-n^2\omega^2)(\tau_w^{-2}+n^2\omega^2)}. \tag{A9}$$

To evaluate the sum S_1 we start with the sum (1.445.6) on page 40 of Ref. [21],

$$\sum_{k=1}^{\infty}\frac{\cos(kx)}{k^2-\alpha^2}=\frac{1}{2\alpha^2}-\frac{\pi}{2}\frac{\cos\{\alpha[(2m+1)\pi-x]\}}{\alpha\sin(\alpha\pi)}, \tag{A10}$$

which is valid if α is not an integer and for $2m\pi\le x\le(2m+2)\pi$. Our case corresponds to $k=n$, $x=2\omega t^*$, $\alpha=\omega_0/\omega$, which gives $m=0$ because $0<t^*<\pi/\omega$. Using the above information in (A10) and differentiating both sides with respect to ω_0,

$$S_1=\frac{\pi}{2\omega\omega_0^3}\frac{\cos(2\omega_0 t^*-\pi\omega_0/\omega)}{\sin(\pi\omega_0/\omega)}+\frac{\pi t^*}{\omega\omega_0^2}\frac{\sin(2\omega_0 t^*-\pi\omega_0/\omega)}{\sin(\pi\omega_0/\omega)}+\frac{\pi^2}{2\omega_0^2\omega^2}\frac{\cos(2\omega_0 t^*)}{\sin^2(\pi\omega_0/\omega)}. \tag{A11}$$

The sum S_2 can be performed by splitting it into two sums with denominators $\omega_0^2-n^2\omega^2$ and $\tau_w^{-2}+n^2\omega^2$ by using the method of partial fractions. The first one can then be obtained from (A10) and the second one can be obtained either from (A10) by changing α to $i\alpha$ or by using the sum (1.445.2) from page 40 of Ref. [21]. In either case, we get

$$S_2=\frac{\pi}{\omega(\tau_w^{-2}+\omega_0^2)}\left[\frac{\cos(2\omega_0 t^*-\pi\omega_0/\omega)}{\omega_0\sin(\pi\omega_0/\omega)}+\frac{\tau_w\cosh[(2t^*-\pi/\omega)/\tau_w]}{\sinh(\pi/\tau_w\omega)}\right]. \tag{A12}$$

Using all of the above tricks, the final result is that the sum in (A1) is given by

$$\frac{\omega E}{\pi\omega_0 M d_1}[\omega_0 t^*-\sin(\omega_0 t^*)\cos(\omega_0 t^*)]+\frac{\omega(E_b-E)}{\pi\omega_b M d_2}(\sinh\theta\cosh\theta-\theta)+(C^{(1)})^2(2d_3^{-1}+d_1^{-1})S_3(\omega_0^2)$$
$$-(C^{(1)})^2(2d_3^{-1}-d_2^{-1})S_3(-\omega_b^2)+(C^{(2)})^2(2d_3^{-1}+d_1^{-1})S_4(\omega_0^2)-(C^{(2)})^2(2d_3^{-1}-d_2^{-1})S_4(-\omega_b^2)$$
$$+C^{(1)}C^{(2)}(2d_3^{-1}+d_1^{-1})S_5(\omega_0^2)-C^{(1)}C^{(2)}(2d_3^{-1}-d_2^{-1})S_5(-\omega_b^2). \tag{A13}$$

Here θ is given by Eq. (31) and $C^{(1)}$, $C^{(2)}$ by Eqs. (A3) and (A4). The constants d_1, d_2, and d_3 are defined by

$$d_1=\tau_w^{-2}+\omega_0^2,\quad d_2=\tau_w^{-2}-\omega_b^2,\quad d_3=\omega_0^2+\omega_b^2, \tag{A14}$$

and the sums S_3, S_4, and S_5 by

$$S_3(\alpha)=\sum_{n=-\infty}^{\infty}\frac{\sin^2(n\omega t^*)}{(\alpha-n^2\omega^2)(\tau_w^{-2}+n^2\omega^2)}, \tag{A15}$$

$$S_4(\alpha)=\sum_{n=-\infty}^{\infty}\frac{n^2\cos^2(n\omega t^*)}{(\alpha-n^2\omega^2)(\tau_w^{-2}+n^2\omega^2)}, \tag{A16}$$

$$S_5(\alpha)=\sum_{n=-\infty}^{\infty}\frac{2n\sin(n\omega t^*)\cos(n\omega t^*)}{(\alpha-n^2\omega^2)(\tau_w^{-2}+n^2\omega^2)}. \tag{A17}$$

These sums can be expressed in terms of S_1 and S_2 as explained before.

We have tested our final result for $\varepsilon_w^{ex}(J)$ in two limits. First of all, in the static case $\tau_w\to 0$, we should get [5] $\varepsilon_w^{ex}(J)=\gamma_w J/\omega$. In this case only the first two terms in (A13) survive and we get the expected result. Secondly when $E\to E_0$, we should get Eq. (A2), irrespective of the magnitude of τ_w. In this case, the only simplification is that $C^{(2)}$ goes to 0. After somewhat lengthy algebra, we find that we indeed get (A2). As mentioned in Sec. III, we evaluate the analytical expressions on a computer for the purpose of calculating the final rate.

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