Quantum phase space function formulation of reactive flux theory

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On the basis of a coherent state representation of quantum noise operator and an ensemble averaging procedure a scheme for quantum Brownian motion has been proposed recently [Banerjee *et al*, Phys. Rev. E **65**, 021109 (2002); **66**, 051105 (2002)]. We extend this approach to formulate reactive flux theory in terms of quantum phase space distribution functions and to derive a time dependent quantum transmission coefficient - a quantum analogue of classical Kramers'-Grote-Hynes coefficient in the spirit of Kohen and Tannor's classical formulation. The theory is valid for arbitrary noise correlation and temperature. The specific forms of this coefficient in the Markovian as well as in the non-Markovian limits have been worked out in detail for intermediate to strong damping regime with an analysis of quantum effects. While the classical transmission coefficient is independent of temperature, its quantum counterpart has significant temperature dependence particularly in the low temperature regime.

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I. INTRODUCTION

The classic work of Kramers[1] on the diffusion model of chemical reactions in 1940 forms the dynamical basis of modern rate theory of activated processes. With the development of ultrafast lasers and time resolved detection techniques since mid seventies it has been possible to monitor the details of the pathways of a reaction on a microscopic scale[2,3]. This has provided a major impetus and also generated a renewal of interest in theoretical development in chemical dynamics, particularly in the problem of reactions in condensed media. Over the decades the field has grown in various new directions, e.g. , extension of Kramers results to non-Markovian regime[4,5,6], generalizations to higher dimensions[7,8], inclusion of complex potentials[9,10], generalization to open systems[11,12,13], analysis of semiclassical and quantum effects[14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29], thermal ratchet[30] and molecular motors[31] etc. These developments have been the subject of several reviews and monographs.We refer to[15,16,17,22].

It is now well known that the rate constant of a chemical reaction may be realized as a typical transport coefficient in phase space. This transport coefficient can be expressed in the form of a Green-Kubo formulae for the flux-flux auto correlation function calculated at the transition state[17,32,33,34,35,36,37] which acts as a dividing surface between the reactant and the product states. The theory of reactive flux has been developed both in classical and quantum mechanical contexts to obtain the rate coefficient of a chemical reaction. Recently Kohen and Tannor[36] have developed a method to calculate the classical rate coefficient and hence the transmission coefficient as a function of time in terms of phase space distribution function in the high friction regime. The method is simple and directly addresses the relevant nonequilibrium dynamics at the barrier top. The theory[36,37] not only recovers the Kramers-Grote-Hynes transmission coefficient in the long time or asymptotic limit but also traces the nature of its transient dynamics and its approach towards the steady state.

The key element of the Kohen-Tannor formulation[36] is that it allows us to express the correlation function with the help of a probability distribution function which describes dynamics of the reaction co-ordinate undergoing Brownian motion in phase space at the barrier top without resorting to a solution of the generalized Fokker-Planck equation. It is worthwhile in this context to ask whether the theory can be extended to quantum domain to include the generic quantum mechanical effects. The essential requirement for such a theory is obviously the quantum phase space distribution function. Very recently, based on a coherent state representation of quantum noise operator and an ensemble averaging procedure, we have developed[24,25,26,27] a c-number quantum generalized Langevin equation. The theory is valid for arbitrary temperature and noise correlation. We extend the scheme in the present context to make use of a true quantum probability distribution function of the relevant dynamical variables in c-numbers and express the rate constant or transmission coefficient accordingly. Our object is thus two-fold, i.e. ,

(i) to express the quantum mechanical rate constant in terms of the c-number quantum phase space functions.

(ii) to derive a time dependent quantum Kramers-Grote-Hynes (KGH) transmission coefficient which is valid for arbitrary noise correlation and temperature for intermediate to strong friction regime.

Two pertinent points are now in order. First, generally speaking the phase space distribution functions used in quantum mechanical contexts, e.g. , in quantum optics are quasi-probability distribution functions like Wigner, or Glauber-Sudarshan functions[38]. They often become singular or negative in the fully quantum domain and can therefore not be regarded as true probability distribution functions as their classical counterparts. We stress that the present formalism is free from such difficulties. Second, the expression for the rate constant as a time integral over flux-flux auto correlation function has been evaluated earlier both analytically and numerically using path integral approaches. Although for equilibrium properties the imaginary time propagator has proved to be very much successful[23], particularly for developing quantum transition state theory[35], it is not easy to extract dynamical information for nonequilibrium problems[22] because of the oscillatory nature of the real time propagator in many situations. The c-number phase space method that we use here, on the other hand, being independent of path integral approach is an alternative for calculation of the rate without these problems.

The outlay of the paper is as follows; After a brief review of our recent scheme for quantum Brownian motion we introduce the conditional probability function of c-numbers at the barrier top and an equilibrium distribution function at the reactant well in Sec.II. In the following section the reactive flux expression for rate constant is formulated in terms of these c-number phase space functions. The time dependent general quantum Kramers-Grote-Hynes transmission coefficient has been derived in the spirit of Kohen and Tannor formalism. We work out in detail the Markovian and non-Markovian limits of this expression. The paper is concluded in Sec.IV.

II. QUANTUM BROWNIAN MOTION ; EVOLUTION OF C-NUMBER PHASE SPACE FUNCTIONS

A. Quantum Langevin equation in c-numbers

The kinetics of a particle undergoing a chemical reaction in a medium can be described by the following generic system-reservoir Hamiltonian

$$H = \frac{\hat{p}^2}{2} + V(\hat{q}) + \sum_j \left\{ \frac{\hat{p}_j^2}{2} + \frac{1}{2}\kappa_j (\hat{q}_j - \hat{q})^2 \right\} \tag{1}$$

Here $\hat{q}$ and $\hat{p}$ are the co-ordinate (here considered as reaction co-ordinate) and momentum operators of the particle, respectively and the set $\{\hat{q}_j, \hat{p}_j\}$ is the set of co-ordinate and momentum operators for the reservoir oscillators linearly coupled to the system through coupling constant κ_j. $V(\hat{q})$ denotes the external potential field which, in general, is nonlinear. The Hamiltonian contains counter-terms quadratic in $\hat{q}$ to ensure the independence of barrier height and coupling constants. The operators follow the usual commutation relations $[\hat{q}, \hat{p}] = i\hbar$ and $[\hat{q}_i, \hat{p}_j] = i\hbar\delta_{ij}$. Over the last several decades the model and its variants have widely served as the fundamental paradigm for quantum Brownian motion in chemical dynamics, condensed matter physics, quantum optics and allied areas within various approximate descriptions. Our primary aim in this section is to search for a true c-number phase space function which describes the evolution of quantum Brownian motion of the particle at the barrier top and its thermalization in the reactant well.

Eliminating the reservoir degrees of freedom in the usual way we obtain the operator Langevin equation for the particle

$$\ddot{\hat{q}} + \int_0^t dt' \gamma(t-t')\dot{\hat{q}}(t') + V'(\hat{q}) = \hat{F}(t) \tag{2}$$

where the noise operator $\hat{F}(t)$ and the memory kernel $\gamma(t)$ are given by

$$\hat{F}(t) = \sum_j \left[\{\hat{q}_j(0) - \hat{q}(0)\}\kappa_j \cos\omega_j t + \hat{p}_j(0)\kappa_j^{1/2} \sin\omega_j t \right] \tag{3}$$

and

$$\gamma(t) = \sum_j \kappa_j \cos\omega_j t$$

or in the continuum limit

$$\gamma(t) = \int_0^\infty \kappa(\omega)\rho(\omega)\cos\omega t \, d\omega \tag{4}$$

with $\kappa_j = \omega_j^2$. The masses have been assumed to be unity. $\rho(\omega)$ represents the density of the reservoir modes.

Eq.(2) is an exact Langevin equation for which the noise properties of $\hat{F}(t)$ can be defined using a suitable canonical initial distribution of bath co-ordinates and momentum. Our first task is to replace it by an equivalent generalized quantum Langevin equation (GQLE) in c-numbers[24,25,26,27]. To achieve this we proceed in two steps. We first carry out the *quantum mechanical average* of Eq.(2).

$$\langle\ddot{\hat{q}}\rangle + \int_0^t dt' \gamma(t-t')\langle\dot{\hat{q}}(t')\rangle + \langle V'(\hat{q})\rangle = \langle\hat{F}(t)\rangle \tag{5}$$

Where the average $\langle....\rangle$ is taken over the initial product separable quantum states of the particle and the bath oscillators at $t=0$, $|\phi\rangle\{|\alpha_1\rangle|\alpha_2\rangle.......|\alpha_N\rangle\}$. Here $|\phi\rangle$ denotes any arbitrary initial state of the particle and $|\alpha_i\rangle$ corresponds to the initial coherent state of the i-th bath oscillator. $|\alpha_i\rangle$ is given by $|\alpha_i\rangle = \exp(-|\alpha_i|^2/2)\sum_{n_i=0}^{\infty}(\alpha_i^{n_i}/\sqrt{n_i!})|n_i\rangle$, α_i being expressed in terms of the mean values of the co-ordinate and momentum of the i-th oscillator, $\langle\hat{q}_i(0)\rangle = (\sqrt{\hbar}/2\omega_i)(\alpha_i + \alpha_i^\star)$ and $\langle\hat{p}_i(0)\rangle = i\sqrt{\hbar\omega_i/2}\,(\alpha_i^\star - \alpha_i)$, respectively. It is important to note that $\langle\hat{F}(t)\rangle$ is a classical-like noise term which, in general, is a nonzero number because of the quantum mechanical averaging over the co-ordinate and momentum operators of the bath oscillators with respect to initial coherent states and arbitrary initial state of the particle and is given by

$$\langle\hat{F}(t)\rangle = \sum_j \left[\{\langle\hat{q}_j(0)\rangle - \langle\hat{q}(0)\rangle\}\kappa_j\cos\omega_j t + \langle\hat{p}_j(0)\rangle\kappa_j^{1/2}\sin\omega_j t\right] \tag{6}$$

It is convenient to write Eq.(5) as follows;

$$\langle\ddot{\hat{q}}\rangle + \int_0^t dt' \; \gamma(t-t')\langle\dot{\hat{q}}(t')\rangle + \langle V'(\hat{q})\rangle = f(t) \tag{7}$$

where we let the quantum mechanical mean value $\langle\hat{F}(t)\rangle = f(t)$. We now turn to the ensemble averaging. To realize $f(t)$ as an effective c-number noise we now assume that the momentum $\langle\hat{p}_j(0)\rangle$ and the co-ordinate $\langle\hat{q}_j(0)\rangle - \langle\hat{q}(0)\rangle$ of the bath oscillators are distributed according to a canonical distribution of Gaussian form as,

$$\mathcal{P}_j = \mathcal{N}\exp\left\{-\frac{[\langle\hat{p}_j(0)\rangle^2 + \kappa_j\{\langle\hat{q}_j(0)\rangle - \langle\hat{q}(0)\rangle\}^2]}{2\hbar\omega_j\left(\bar{n}_j + \frac{1}{2}\right)}\right\} \tag{8}$$

so that for any quantum mean value $\mathcal{O}_j(\langle\hat{p}_j(0)\rangle, \{\langle\hat{q}_j(0)\rangle - \langle\hat{q}(0)\rangle\})$, the statistical average $\langle....\rangle_s$ is

$$\langle\mathcal{O}_j\rangle_s = \int \mathcal{O}_j \; \mathcal{P}_j \; d\langle\hat{p}_j(0)\rangle \; d\{\langle\hat{q}_j(0)\rangle - \langle\hat{q}(0)\rangle\} \tag{9}$$

Here $\bar{n}_j$ indicates the average thermal photon number of the j-th oscillator at temperature T and is given by Bose-Einstein distribution $\bar{n}_j = 1/[\exp(\hbar\omega_j/kT) - 1]$ and $\mathcal{N}$ is the normalization constant.

The distribution Eq.(8) and the definition of the statistical average over quantum mechanical mean values Eq.(9) imply that $f(t)$ must satisfy

$$\langle f(t)\rangle_s = 0 \tag{10}$$

and

$$\langle f(t)f(t')\rangle_s = \frac{1}{2}\sum_j \kappa_j \; \hbar\omega_j \left(\coth\frac{\hbar\omega_j}{2kT}\right)\cos\omega_j(t-t')$$

or in the continuum limit

$$\begin{aligned}\langle f(t)f(t')\rangle_s &= \frac{1}{2}\int_0^\infty d\omega\ \kappa(\omega)\ \rho(\omega)\ \hbar\omega \left(\coth\frac{\hbar\omega}{2kT}\right)\cos\omega(t-t') \\ &\equiv c(t-t') \end{aligned} \tag{11}$$

That is, c-number noise $f(t)$ is such that it is zero-centered and satisfies standard fluctuation-dissipation relation as known in the literature.

We now add the force term $V'(\langle\hat{q}\rangle)$ on both sides of the Eq.(7) and rearrange it to obtain

$$\ddot{q}(t) + V'(q) + \int_0^t dt'\ \gamma(t-t')\ \dot{q}(t') = f(t) + Q(t) \tag{12}$$

where we put $\langle\hat{q}(t)\rangle = q(t)$ and $\langle\dot{\hat{q}}(t)\rangle = p(t)$; $q(t)$ and $p(t)$ being quantum mechanical mean values and also

$$Q(t) = V'(q) - \langle V'(\hat{q})\rangle \tag{13}$$

represents the quantum correction to classical potential.

Eq.(12) offers a simple interpretation. This is that GQLE Eq.(12) is governed by a c-number quantum noise $f(t)$ due to the heat bath, characterized by the properties Eq.(10), Eq.(11) and a quantum correction term $Q(t)$ characteristic of nonlinearity of the potential. Our general results contain $Q(t)$ in all orders formally. However for a practical calculation we need a recipe for calculation of $Q(t)$. This has been discussed earlier in several contexts[24,25,26,27,39,40]. For the present purpose we summarize it as follows:

Referring to the quantum mechanics of the system in the Heisenberg picture one may write,

$$\begin{aligned}\hat{q}(t) &= \langle\hat{q}(t)\rangle + \delta\hat{q}(t) \\ \hat{p}(t) &= \langle\hat{p}(t)\rangle + \delta\hat{p}(t)\end{aligned} \tag{14}$$

$\delta\hat{q}(t)$ and $\delta\hat{p}(t)$ are the operators signifying quantum corrections around the corresponding quantum mechanical mean values q and p. By construction $\langle\delta\hat{q}\rangle = \langle\delta\hat{p}\rangle = 0$ and $[\delta\hat{q}, \delta\hat{p}] = i\hbar$. Using Eq.(14) in $\langle V'(\hat{q})\rangle$ and a Taylor series expansion around $\langle\hat{q}\rangle$ it is possible to express $Q(t)$ as

$$Q(t) = -\sum_{n\geq 2}\frac{1}{n!}V^{(n+1)}(q)\langle\delta\hat{q}^n(t)\rangle \tag{15}$$

Here $V^{(n)}(q)$ is the n-th derivative of the potential $V(q)$. To second order $Q(t)$ is given by $Q(t) = -\frac{1}{2}V'''(q)\langle\delta\hat{q}^2(t)\rangle$ where $q(t)$ and $\langle\delta\hat{q}^2(t)\rangle$ can be obtained as explicit functions of time by solving following set of approximate coupled equations Eq.(16) to Eq.(18) together with Eq.(12)

$$\langle\dot{\delta\hat{q}^2}\rangle = \langle\delta\hat{q}\delta\hat{p} + \delta\hat{p}\delta\hat{q}\rangle \tag{16}$$

$$\langle\delta\hat{q}\delta\hat{p} \dot{+} \delta\hat{p}\delta\hat{q}\rangle = 2\langle\delta\hat{p}^2\rangle - 2V''(q)\langle\delta\hat{q}^2\rangle \tag{17}$$

$$\langle\dot{\delta\hat{p}^2}\rangle = -V''(q)\langle\delta\hat{q}\delta\hat{p} + \delta\hat{p}\delta\hat{q}\rangle \tag{18}$$

While the above set of equations provide analytic solutions containing lowest order quantum corrections, the successive improvement of $Q(t)$ can be achieved by incorporating higher order contribution due to potential $V(q)$ and the higher order effect of dissipation on the quantum correction terms. In Appendix A we have derived the equations for quantum corrections upto forth oder[39]. Under very special circumstances, it has been possible to include quantum effects to all orders[27,40]. The present theory thus takes into account of the anharmonicity as an integral part of the treatment. This is somewhat different from usual classical theories where anharmonicity is incorporated from outside as a finite barrier corrections[41,42]. We mention here that centroid molecular dynamics simulation methods have been developed to calculate the expression for rate constant which is related to flux-flux correlation functions involving two nonlinear operators within bilinear system-reservoir coupling[43]. Apart from anharmonicity of the system potential it is also possible to consider nonlinear coupling, e.g. , $\sum_j \frac{1}{2}\ \kappa_j\ f(\hat{q})\ \hat{q}_j$ (beyond bilinear) between the system and the reservoir. In the present context we, however, envisage two difficulties. First, the potential in which the particle moves gets significantly modified because of the absence of any counter term in the Hamiltonian as in Eq.(1). Secondly, the operator Langevin equation of motion would contain multiplicative noise for which a linear dissipation fails to satisfy the usual fluctuation-dissipation relation. Because of these reasons we confine ourselves within traditional bilinear coupling. The method can, however, be readily extended to anharmonic bath comprising, say, of Morse oscillators or of two level systems, for which coherent states are well known (Morse oscillator is amenable to a theoretical description within SU(2) Lie algebra and the associated coherent states[51], while the two-level system in terms of Pauli matrix and Radcliffe coherent states[52]) for constructing quantum Langevin equation since the quantum mechanical averaging with these states can be computed exactly in the same way as we proceeded from Eq.(2) to obtain Eq.(5). The present approach has recently been utilized by us to derive[24,26] generalized quantum Kramers' equation for calculation of escape rate over the barrier by extending the flux-over-population method to quantum domain.

B. Conditional probability function of c-numbers at the barrier top

We now show that the present scheme allows us to derive a quantum conditional probability function in c-numbers $W(q,p,t;q_0,p_0,t=0)$ for an ensemble of trajectories starting from a specific initial condition $q=q_0$, $p=p_0$ at $t=0$ and following the quantum Langevin dynamics Eq.(12). Since we will be primarily concerned with the reactive flux at the barrier top located at $q=q_0(=0)$ it is convenient to linearize the potential $V(q)$ at this point as $V(q)=V(0)-\frac{1}{2}\omega_b^2 q^2$ where $\omega_b^2 = V''|_{q_0=0}$ refers to the oscillator frequency of the inverted well at $q=q_0$. We are then lead to the following Langevin equation;

$$\ddot{q} - \omega_b^2 q + \int_0^t dt'\ \gamma(t-t')\ \dot{q}(t') = f(t) + Q(t) \tag{19}$$

Laplace transform of Eq.(19) yields the formal solutions for $q(t)$ and $p(t)$ as follows;

$$q(t) = \langle q(t)\rangle_s + \int_0^t C_v(t-\tau) f(\tau)\ d\tau \tag{20}$$

$$p(t) = \langle p(t)\rangle_s + \int_0^t \dot{C}_v(t-\tau) f(\tau)\ d\tau \tag{21}$$

where

$$\langle q(t)\rangle_s = p_0\ C_v(t) + q_0\ C_q(t) + G(t) \tag{22}$$

$$\langle p(t)\rangle_s = p_0\ \dot{C}_v(t) + q_0\ \dot{C}_q(t) + \dot{G}(t) \tag{23}$$

$$G(t) = \int_0^t C_v(t-\tau)\ Q(\tau)\ d\tau \tag{24}$$

$$C_q(t) = 1 + \omega_b^2 \int_0^t C_v(\tau)\ d\tau \tag{25}$$

Here $C_v(t)$ is the inverse Laplace transform of $\tilde{C}_v(\mu)$, i.e.

$$C_v(t) = L^{-1}\left[\mu^2 + \mu\ \tilde{\gamma}(\mu) - \omega_b^2\right]^{-1} \tag{26}$$

with

$$\tilde{\gamma}(\mu) = \int_0^t dt\, \gamma(t)\, e^{-\mu t} \tag{27}$$

the Laplace transform of $\gamma(t)$. Several remarks are now in order.

First, the solutions of Eq.(20) and Eq.(21) of the Langevin equation Eq.(12) are the quantum mechanical mean values distributed around their statistical average $\langle q \rangle_s$ and $\langle p \rangle_s$. The distribution is due to Gaussian, c-number quantum noise $f(t)$ which obeys Eq.(10) and Eq.(11).

Second, the averages $\langle q \rangle_s$ and $\langle p \rangle_s$ not only depend on the relaxation functions $C_v(t)$ and $C_q(t)$ in the same way as in the corresponding classical theory[36] but also on the convolution integral $G(t)$ which is a quantum contribution and takes care of the interplay of dissipation and nonlinearity in the dynamics. It is important to note that although we have linearized the potential $V(q)$, $Q(t)$ remains finite and nonzero. This is because linearization involves local dynamics around a specific q (say, around $q = 0$ for the barrier top) which is a quantum mechanical mean value $\langle \hat{q} \rangle$. $Q(t)$ as expressed in Eq.(15) implies quantum fluctuation around this mean value manifested as shifts in $\langle q \rangle_s$ and $\langle p \rangle_s$ as shown in Eq.(22) and Eq.(23) respectively. Making the quantum fluctuations $\langle \delta \hat{q}^n(t) \rangle$ or $Q(t)$ equal to zero would mean that the quantum mechanical position of the particle is exactly specified. Thus nonzero finite quantum fluctuation around $q = 0$ takes care of uncertainty relation. In other words to consider the conditional probability distribution function which originates as a δ-function in position (means quantum mechanical mean) at the barrier top, we must have to associate a finite minimum quantum fluctuation or uncertainty around this point.

Third, since no approximation has been made on $Q(t)$, the solutions Eq.(20) and Eq.(21) for $q(t)$ and $p(t)$ formally take care of quantum effects to all orders. In actual practice, however, they can be calculated order by order to a high degree of accuracy.

Fourth, the quantum effects enter into the dynamics in two different ways. The quantum nature of the system is manifested through nonlinearity of the potential while the heat bath imparts quantum noise in a thermal environment.

$f(t)$ is a c-number Gaussian random process. Since the sum of the random processes is Gaussian, so is the integral in Eq.(20) and Eq.(21) we conclude that $q - \langle q \rangle_s$ and $p - \langle p \rangle_s$ are Gaussian random processes. Therefore the first and the second moments suffice to determine the distribution function. Making use of Eq.(20) and Eq.(21) we construct the second moments of $q - \langle q \rangle_s \left(= \int_0^t C_v(t-\tau) f(\tau)\, d\tau \right)$ and $p - \langle p \rangle_s \left(= \int_0^t \dot{C}_v(t-\tau) f(\tau)\, d\tau \right)$ as

$$A_{11}(t) = \langle (q - \langle q \rangle_s)^2 \rangle_s = 2 \int_0^t C_v(t_1)\, dt_1 \int_0^{t_1} C_v(t_2)\, c(t_1 - t_2)\, dt_2 \tag{28}$$

$$A_{22}(t) = \langle (p - \langle p \rangle_s)^2 \rangle_s = 2 \int_0^t \dot{C}_v(t_1)\, dt_1 \int_0^{t_1} \dot{C}_v(t_2)\, c(t_1 - t_2)\, dt_2 \tag{29}$$

$$A_{12}(t) = A_{21}(t) = \langle\, (q - \langle q \rangle_s)(p - \langle p \rangle_s)\, \rangle_s = 2 \int_0^t C_v(t_1)\, dt_1 \int_0^{t_1} \dot{C}_v(t_2)\, c(t_1 - t_2)\, dt_2 \tag{30}$$

We are now in a position to write down the probability distribution function of q, p conditional on $q(t = 0) = q_0$ and $p(t = 0) = p_0$

$$\begin{aligned} W(q, p, t; q_0, p_0, t = 0) \;&=\; \frac{1}{2\pi (detA)^{1/2}} \times \exp\left[-\frac{1}{2(detA)} \left\{ A_{22}(q - \langle q \rangle_s)^2 \right.\right. \\ &-\; \left.\left. 2A_{12}(q - \langle q \rangle_s)(p - \langle p \rangle_s) + A_{11}(p - \langle p \rangle_s)^2 \right\} \right] \end{aligned} \tag{31}$$

Here $detA$ refers to the determinant of the matrix A. The conditional probability W therefore describes the transition probability in a c-number quantum phase space. Two remarks are pertinent at this point. First, it is easy to check that the W reduces to the classical distribution function in the limit $\hbar \to 0$, i.e. , when $G(t) \to 0$ and $\frac{\hbar \omega_b}{2} \coth(\hbar \omega_b / 2kT)$ goes over to kT. Second, since $W(q, p, t; q_0, p_0, t = 0)$ concerns dynamics at the barrier top where strong nonequilibrium situation prevails, W does not go over to an equilibrium distribution because of hyperbolic nature of the trajectories emanating from $q = q_0 = 0$. However, this phase space distribution function serves as a basis for calculation of average of the relevant dynamical quantities at the barrier top.

C. Equilibrium distribution in the reactant well

In addition to the distribution at the barrier top $W(q,p,t;q_0,p_0,t=0)$ it is necessary to consider further the equilibrium distribution of the particles in the reactant well. As usual a good description of the kinetics can be obtained by linearizing the potential $V(q)$ at the bottom of the well (say at $q=0$) so that $V(q)=V(0)+\frac{1}{2}\omega_0^2 q^2$ where ω_0 corresponds the frequency at the bottom of the reactant well. The Langevin dynamics can be obtained from Eq.(19) with the replacement of $-\omega_b^2$ by ω_0^2. The essential changes that are needed for the solution of $q(t)$ and $p(t)$ are

$$C_v(t) = L^{-1}\tilde{C}(\mu) = L^{-1}\left[\mu^2 + \mu\ \tilde{\gamma}(\mu) + \omega_0^2\right]^{-1} \tag{32}$$

$$C_q(t) = 1 - \omega_0^2 \int_0^t C_v(\tau)\ d\tau \tag{33}$$

The first and second moments of the distribution W can therefore be calculated by employing the relations Eq.(20) to Eq.(24) and Eq.(28) to Eq.(30). Since $W(q,p,t;q_0,p_0,t=0)$ pertains to the dynamics in the reactant well where the trajectories evolve around a stable elliptic fixed point, the distribution W eventually reaches an equilibrium thermal distribution in the long time limit, i.e. ,

$$\mathcal{L}t_{t\to\infty} W(q,p,t;q_0,p_0,t=0) = W_{eqm}(q,p) \tag{34}$$

Since an equilibrium distribution does not depend on the way in which the final state is reached, one may consider the Markovian limit for simplicity but without any loss of generality. In this limit the density distribution of the reservoir modes is flat, i.e. , $\kappa(\omega)\rho(\omega) = 2\gamma/\pi$, γ being dissipation constant. This results in

$$\gamma(t) = 2\ \gamma\ \delta(t) \tag{35}$$

and

$$c(t) = \frac{1}{2}\ \gamma\ \hbar\omega_0\ \coth\left(\frac{\hbar\omega_0}{2kT}\right)\ \delta(t) \tag{36}$$

from Eq.(4) and Eq.(11), respectively. From Eq.(35) we have $\tilde{\gamma}(\mu)=\gamma$ which when put in Eq.(32) gives after inverse Laplace transform

$$C_v(t) = \frac{\left(e^{\mu_1' t} - e^{\mu_2' t}\right)}{2\omega_1'} \tag{37}$$

where $\mu_1' = -\frac{\gamma}{2} + \omega_1'$ and $\mu_2' = -\frac{\gamma}{2} - \omega_1'$ with $\omega_1' = \sqrt{\frac{\gamma^2}{4} - \omega_0^2}$. By Eq.(33) we obtain

$$C_q(t) = 1 - \frac{\omega_0^2}{2\omega_1'}\left[\frac{1}{\mu_1'}(e^{\mu_1' t} - 1) - \frac{1}{\mu_2'}(e^{\mu_2' t} - 1)\right] \tag{38}$$

It is easy to check the stationary limits for the model

$$\mathcal{L}t_{t\to\infty} C_v(t) \ = \ 0 \qquad \mathcal{L}t_{t\to\infty} C_q(t) = 0 \tag{39}$$

$$\mathcal{L}t_{t\to\infty} \dot{C}_v(t) \ = \ 0 \qquad \mathcal{L}t_{t\to\infty} \dot{C}_q(t) = 0 \tag{40}$$

An important quantity that contains quantum contribution due to the system is $G(t)$ as defined in Eq.(24). Putting Eq.(37) in Eq.(24) we write

$$G(t) = \frac{1}{2\omega_1'}\left[\int_0^t e^{\mu_1' \tau} Q(t-\tau)\ d\tau - \int_0^t e^{\mu_2' \tau} Q(t-\tau)\ d\tau\right] \tag{41}$$

For the bound system, i.e. , in the neighborhood of the minimum of the well the solutions $q(t)$ and $\langle \delta \hat{q}^n(t) \rangle$, in general, are oscillating in nature, while the exponentials in Eq.(41) are decaying in time. Keeping in mind the nature of the system, and expanding $Q(t-\tau)$ in Taylor series as $Q(t-\tau) = \sum_m \frac{(-1)^m}{m!} \, Q^m(t) \, \tau^m$, Q^m being the m-th time derivative of $Q(t)$, the long time limit of $G(t)$ is given by

$$\mathcal{L}t_{t\to\infty} G(t) = \frac{1}{2\omega_1'} \left[\sum_m (-1)^m Q^m(t) \left(\frac{1}{(-\mu_1')^m} - \frac{1}{(-\mu_2')^m} \right) \right] \tag{42}$$

Since from Eq.(15) the leading order quantum correction is given by $Q(t) = -\frac{1}{2} V'''(q) \langle \delta \hat{q}(t)^2 \rangle$ it is now easy to check that for the time derivative terms in Eq.(42), this correction leads to (and also for higher order correction terms in $Q(t)$),

$$\mathcal{L}t_{t\to\infty} G(t) = 0 \tag{43}$$

for quartic nonlinearity, where we have made use of the relations Eq.(22) and Eq.(23). Similarly one may show

$$\mathcal{L}t_{t\to\infty} \dot{G}(t) = 0 \tag{44}$$

By virtue of the relations Eq.(39), Eq.(40), Eq.(43) and Eq.(44) we have

$$\langle q \rangle_s = 0 \qquad \langle p \rangle_s = 0 \tag{45}$$

Furthermore making use of the relation Eq.(36) for $c(t)$ we obtain from Eq.(28) to Eq.(30) the following expressions for the second moments.

$$A_{11}(t) \;=\; \gamma \, \hbar\omega_0 \coth\left(\frac{\hbar\omega_0}{2kT}\right) \int_0^t C_v^2(t_1) \, dt_1 \tag{46}$$

$$A_{22}(t) \;=\; \gamma \, \hbar\omega_0 \coth\left(\frac{\hbar\omega_0}{2kT}\right) \int_0^t \dot{C}_v^2(t_1) \, dt_1 \tag{47}$$

$$A_{12}(t) = A_{21}(t) \;=\; \gamma \, \hbar\omega_0 \coth\left(\frac{\hbar\omega_0}{2kT}\right) \int_0^t C_v(t_1) \, \dot{C}_v(t_1) \, dt_1 \tag{48}$$

Putting Eq.(37) in Eq.(46) to Eq.(48) we obtain the long time limits of the second moments as

$$\mathcal{L}t_{t\to\infty} A_{11}(t) \;=\; \frac{\hbar}{2\omega_0} \coth\left(\frac{\hbar\omega_0}{2kT}\right) \tag{49}$$

$$\mathcal{L}t_{t\to\infty} A_{22}(t) \;=\; \frac{\hbar\omega_0}{2} \coth\left(\frac{\hbar\omega_0}{2kT}\right) \tag{50}$$

$$\mathcal{L}t_{t\to\infty} A_{12}(t) \;=\; \mathcal{L}t_{t\to\infty} A_{21}(t) = 0 \tag{51}$$

Next we use the relations Eq.(45) and Eq.(49) to Eq.(51) in Eq.(31) to obtain the equilibrium distribution of quantum mechanical mean values, q, p as

$$W_{eqm}(q,p) = Z^{-1} \exp\left[- \frac{\frac{p^2}{2} + V(q)}{\frac{\hbar\omega_0}{2} \coth\left(\frac{\hbar\omega_0}{2kT}\right)} \right] \tag{52}$$

where Z^{-1} is the normalization constant and $V(q)$ has the linearized form in the neighborhood of the bottom of the reactant well characterized by the frequency ω_0. The width of the distribution $\frac{\hbar\omega_0}{2} \coth\left(\frac{\hbar\omega_0}{2kT}\right)$ reduces to kT in the classical limit and one obtains the usual Maxwell-Boltzmann distribution. We thus note that Eq.(52) has the same form as Eq.(8) (since, $\overline{n}(x) + 1/2 = \frac{1}{2}\coth(x/2)$). In fact since theq potential at the reactant well is assumed to the harmonic, it seems consistent to use the same ansatz that was used for the harmonic bath modes. This has turned out to be the case.

The c-number conditional probability distribution $W(q, p, t; q_0, p_0, t = 0)$ describing the dynamics at the barrier top and the thermal distribution $W_{eqm}(q, p)$ describing equilibrium in the reactant well are the two main results of this section. They are primary elements for calculation of statistical averages used in the expression for reactive flux that follows in the next section.

III. C-NUMBER PHASE SPACE FUNCTION FORMULATION OF REACTIVE FLUX THEORY

A. A general expression for quantum transmission coefficient

We now consider q as the reaction co-ordinate and the potential $V(q)$ defines the dividing surface conveniently located at the transition state $q = q_0$ which separates the reactant state from the product state. While the reactant particles are thermally equilibriated deep inside the reactant well strong nonequilibrium situation prevails at $q = q_0$. The key element in the reactive flux formulation is that the nonequilibrium concentration relaxes to the equilibrium concentration on a timescale at which the equilibrium correlation function decays. Based on a timescale t obeying $\frac{1}{\Gamma} \gg t \gg \tau_c$ where $\frac{1}{\Gamma}$ is the decay time of equilibrium fluctuation and τ_c is correlation time, the reactive flux expression for rate coefficient in the form of Green-Kubo transport coefficient has been derived by various workers[32,33,34,35,36,37]. Our aim in this section is to provide a *c-number quantum phase space* representation of the rate coefficient. The present formulation is a simple quantum translation of the reactive flux formulation advocated by Kohen and Tannor[36] a few years ago.

In the spirit of classical reactive flux theory the quantum rate coefficient $k(t)$ can be expressed in terms of the following correlation function

$$k(t) = \frac{\langle \dot{\theta}_P(q_0)\ \theta_P[q(q_0, p_0, t)] \rangle_{qs}}{\langle \theta_R(q_0) \rangle_{qs}} \tag{53}$$

$$= \frac{\langle p_0\ \delta(q_0)\ \theta_P[q(q_0, p_0, t)] \rangle_{qs}}{\langle \theta_R(q_0) \rangle_{qs}} \tag{54}$$

Here q is the quantum mechanical mean values of reaction co-ordinate and p is the corresponding momentum. $\theta_P[q]$ is a step function implying 1 if $q > 0$ and 0 otherwise. Noting that R and P refer to the reactant and transition states, respectively, we have $\theta_R + \theta_P = 1$. q_0, p_0 correspond to initial co-ordinate (at the barrier top; $q = q_0 = 0$) and momentum, respectively. The averaging $\langle ... \rangle_{qs}$ is carried over an initial equilibrium distribution, which in our case is the c-number quantum distribution $W_{eqm}(q, p)$ of q, p as given by Eq.(52). The subscript 'qs' in the average is labeled to make a distinction from its classical counterpart. Thus when written explicitly in terms of Eq.(52), Eq.(54) reduces to the following form

$$k(t) = \frac{Z^{-1}}{\langle \theta_R(q_0) \rangle_{qs}} \int_{-\infty}^{+\infty} dq_0 \int_{-\infty}^{+\infty} dp_0\ \exp\left[-\frac{\frac{p_0^2}{2} + V(q_0)}{\frac{\hbar\omega_0}{2} \coth\left(\frac{\hbar\omega_0}{2kT}\right)} \right] p_0\ \delta(q_0)\ \theta_P[q(q_0, p_0, t)] \tag{55}$$

For a single realization of a stochastic trajectory the characteristic function $\theta_P[q(q_0, p_0, t)]$ is either 0 or 1. However for an ensemble of trajectories starting from q_0, p_0, $\theta_P[q]$ must be replaced by an average $\overline{\theta_P[q]}$, which may assume any value between 0 and 1. In explicit form $\overline{\theta_P[q]}$ signifies an integral over the c-number quantum conditional probability distribution function $W(q, p, t; q_0, p_0, t = 0)$ for the ensemble of particles as given by Eq.(31) so that

$$\overline{\theta_P[q(q_0, p_0, t)]} = \chi(p_0, t) = \int_0^{+\infty} dq \int_{-\infty}^{+\infty} dp\ W(q, p, t; q_0 = 0, p_0, t = 0) \tag{56}$$

χ is the usual "reactivity index" and takes care of recrossing the transition state. With this replacement of $\theta_P[q(q_0, p_0, t)]$ by its average according to Eq.(56) we obtain the expression for quantum rate coefficient as

$$\begin{aligned} k(t) &= \frac{Z^{-1}}{\langle \theta_R(q_0) \rangle_{qs}} \int_{-\infty}^{+\infty} dq_0 \int_{-\infty}^{+\infty} dp_0\ \exp\left[-\frac{\frac{p_0^2}{2} + V(q_0)}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})} \right] p_0\ \delta(q_0)\ \chi(q_0 = 0, p_0, t) \\ &= \frac{Z^{-1}}{\langle \theta_R(q_0) \rangle_{qs}} \int_{-\infty}^{+\infty} dp_0\ p_0\ \exp\left[-\frac{\frac{p_0^2}{2} + V(q_0 = 0)}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})} \right] \chi(q_0 = 0, p_0, t) \end{aligned} \tag{57}$$

In order to extract out the dynamical contribution to the rate coefficient it is convenient to define the latter as

$$k(t) = \kappa(t)\ k_{QTST} \tag{58}$$

where $\kappa(t)$ is the quantum transmission coefficient and k_{QTST} corresponds to the rate coefficient according to transition state theory. In the following we outline an expression for k_{QTST}.

It has been shown that thermalization of the reactant in the well can be described by the distribution Eq.(52). Assuming that this equilibrium distribution holds good even at the barrier top q_0 Eq.(52) reduces to

$$W_{eqm}(q_0 = 0, p) = Z^{-1} \exp\left[-\frac{\frac{p^2}{2} + V(q_0 = 0)}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})}\right] \tag{59}$$

and we may calculate the rate coefficient as

$$k_{QTST} = \int_0^{\infty} p\, W_{eqm}(q_0 = 0, p)\, dp \tag{60}$$

which represents the positive average velocity of the particles at the barrier top. The recrossing of the trajectories is therefore completely ignored. Explicit integration in Eq.(60) using Eq.(59) yields

$$k_{QTST} = Z^{-1}\hbar\omega_0(\bar{n}_0 + \frac{1}{2}) \exp\left[-\frac{V(q_0 = 0)}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})}\right] \tag{61}$$

We now note that the total reactant concentration in the left well is given by equilibrium average over the characteristic function $\langle\theta_R(q_0)\rangle_{qs}$ which is obtained by

$$\langle\theta_R(q_0)\rangle_{qs} = \mathcal{L}t_{a\to\infty} \int_{q'-a}^{q'+a} dq \int_{-\infty}^{+\infty} W_{eqm}(q,\ p) \tag{62}$$

where $W_{eqm}(q,p)$ is given by Eq.(52) with the linearization of the potential well at $q = q'$ such that $V(q) = V(q') + \frac{1}{2}\,\omega_0^2\,(q - q')^2$. By setting $V(q') = 0$ and calculating the normalization constant $Z^{-1} = 2\pi\hbar(\bar{n}_0 + \frac{1}{2})$, we have

$$\langle\theta_R\rangle_{qs} = 1 \tag{63}$$

Now putting the value of $\langle\theta_R\rangle_{qs}$ in Eq.(57) and dividing $k(t)$ by k_{QTST} as given in Eq.(61) we obtain the expression for quantum time dependent transmission coefficient $\kappa(t)$ as;

$$\kappa(t) = \frac{1}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})} \int_{-\infty}^{+\infty} p_0 \exp\left[-\frac{\frac{p_0^2}{2}}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})}\right] \chi(q_0 = 0, p_0, t)\, dp_0 \tag{64}$$

where the fractional reactivity index χ is given by Eq.(56), i.e. ;

$$\chi(p_0, t) = \int_0^{+\infty} dq \int_{-\infty}^{+\infty} dp\, W(q, p, t; q_0 = 0, p_0, t = 0) \tag{65}$$

On explicit integration over p using Eq.(31) the above expression gives

$$\chi(p_0, t) = \frac{1}{(2\pi A_{11})^{1/2}} \int_0^{\infty} dq\ \exp\left[-\frac{(q - \langle q\rangle_s)^2}{2A_{11}}\right] \tag{66}$$

Furthermore with the transformation variables $h = \frac{q - \langle q\rangle_s}{2A_{11}}$, Eq.(66) reduces to

$$\chi(p_0, t) = \frac{1}{\pi^{1/2}} \int_{-\frac{\langle q(t)\rangle_s}{[2A_{11}(t)]^{1/2}}}^{\infty} dh\ e^{-h^2} \tag{67}$$

The expression for $\kappa(t)$ is given by

$$\kappa(t) = \frac{1}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})} \int_{-\infty}^{+\infty} dp_0 \, p_0 \, \exp\left[- \frac{\frac{p_0^2}{2}}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})} \right] \left[\frac{1}{\pi^{1/2}} \int_{-\frac{\langle q(t) \rangle_s}{[2A_{11}(t)]^{1/2}}}^{\infty} dh \, e^{-h^2} \right] \tag{68}$$

The primary quantities that determine $\kappa(t)$ are therefore $\langle q(t) \rangle_s$ and $A_{11}(t)$ as given by Eq.(22) and Eq.(28), respectively, pertaining to the dynamics at the barrier top. Putting the value of $\langle q(t) \rangle_s$ in the lower limit of the second integral and carrying out integration by parts we obtain the general expression for quantum transmission coefficient $\kappa(t)$ as follows;

$$\kappa(t) = \frac{C_v(t)}{\left\{ C_v^2(t) + \frac{A_{11}(t)}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})} \right\}^{1/2}} \exp\left[- \frac{G^2(t)}{2\{ C_v^2(t) \, \hbar\omega_0(\bar{n}_0 + \frac{1}{2}) + A_{11}(t) \}} \right] \tag{69}$$

The expression Eq.(69) is the direct quantum generalization of Kohen-Tannor formulae[36] for classical time dependent transmission coefficient. The classical formulae can be recovered in the limit $kT \gg \hbar\omega_0$, so that $\hbar\omega_0(\bar{n}_0 + \frac{1}{2})$ and $\hbar\omega_b(\bar{n}_b + \frac{1}{2})$ reduce to kT and $G(t) \to 0$. A few pertinent points are to be noted: First, since no approximation has been made on the order of quantum correction in $G(t)$, the expression takes care of quantum effects to all orders and thus retains its validity even in the limit $T \to 0$, i.e. , in the vacuum regime. Second, since we have not assumed any specific form of the density of modes of the bath oscillators so that $\kappa(\omega)\rho(\omega)$ is arbitrary, the theory developed so far is equipped to deal with arbitrary noise correlation. Third, it is important to note that important quantities in the expression Eq.(69), $C_v(t)$, $A_{11}(t)$, and $G(t)$ are the key elements required for calculation of the dynamics of transmission coefficient $\kappa(t)$. While $C_v(t)$ is the same as in the classical theory, $A_{11}(t)$ and $G(t)$ are quantum mechanical objects. $A_{11}(t)$ carries the imprints of quantum fluctuation-dissipation relationship characterizing the quantum nature of the heat bath. $G(t)$ on the other hand, as mentioned earlier is a reflection of the characteristic of the nonlinear potential. The interplay of the dissipation with the nonlinearity of the system is expressed through this convolution integral. A complete calculation of the transmission coefficient thus requires the explicit knowledge of these three quantities.

In order to proceed further it is necessary to specify the nature of the time dependent friction $\gamma(t)$. This is crucially dependent on the distribution of the density of modes of the bath oscillators. In the present case we assume a specific form of Lorentian type, i.e. ;

$$\kappa(\omega)\rho(\omega) = \frac{2}{\pi} \left(\frac{A}{1 + \omega^2 \, \tau_c^2} \right) \tag{70}$$

where A is the damping constant in the Markovian limit and τ_c is the correlation time. This form of density by virtue of Eq.(4) results in,

$$\begin{aligned} \gamma(t) &= \frac{A}{\tau_c} e^{-t/\tau_c} \\ &= A \, \alpha \, e^{-\alpha t} \end{aligned} \tag{71}$$

where $\alpha = 1/\tau_c$.

Depending on τ_c we consider two different limits; Markovian and non-Markovian friction. We consider the former case first.

B. Markovian friction

For $\alpha \to \infty$ or $\tau_c \to 0$, we have $\kappa(\omega)\rho(\omega) = 2A/\pi$; $\gamma(t)$ and its Laplace transform thus reduce to

$$\gamma(t) = 2 \, A \, \delta(t)$$

and

$$\tilde{\gamma}(\mu) = A \tag{72}$$

respectively. According to Eq.(26) $C_v(t)$ is then given by

$$C_v(t) = \frac{e^{\mu_1 t} - e^{\mu_2 t}}{2\omega_1} \tag{73}$$

where $\mu_{1,2} = -\frac{A}{2} \pm \omega_1$ and $\omega_1 = \sqrt{\frac{A^2}{4} + \omega_b^2}$. Furthermore the correlation function as given by Eq.(11) yields

$$c(t_1 - t_2) = \frac{1}{2}\, A\, \hbar\omega_b \coth\left(\frac{\hbar\omega_b}{2kT}\right) \delta(t_1 - t_2) \tag{74}$$

Making use of the last two relations for $C_v(t)$ and $c(t_1 - t_2)$ for the barrier top in Eq.(28) we obtain

$$A_{11}(t) = \frac{A}{2\omega_1^2}\, \hbar\omega_b(\bar{n}_b + \frac{1}{2}) \left[\frac{1}{2\mu_1} e^{2\mu_1 t} + \frac{1}{2\mu_2} e^{2\mu_2 t} + \frac{2}{A} e^{-At} - \frac{2\omega_1^2}{\omega_b^2 A}\right] \tag{75}$$

Having known $C_v(t)$ and $A_{11}(t)$ in the Markovian limit we are in a position to use them in the general expression for quantum transmission coefficient Eq.(69) to obtain,

$$\begin{aligned}\kappa(t) = {} & \frac{e^{\mu_1 t} - e^{\mu_2 t}}{\left\{ (e^{2\mu_1 t} + e^{2\mu_2 t} - 2e^{-At}) + \frac{2A\hbar\omega_b(\bar{n}_b + \frac{1}{2})}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})} \left[\frac{1}{2\mu_1} e^{2\mu_1 t} + \frac{1}{2\mu_2} e^{2\mu_2 t} + \frac{2}{A} e^{-At} - \frac{2\omega_1^2}{\omega_b^2 A}\right] \right\}^{1/2}} \\ & \times \exp\left[- \frac{G^2(t)}{\frac{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})}{2\omega_1^2} \left[(e^{2\mu_1 t} + e^{2\mu_2 t} - 2e^{-At}) + \frac{2A\hbar\omega_b(\bar{n}_b + \frac{1}{2})}{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})} \left[\frac{1}{2\mu_1} e^{2\mu_1 t} + \frac{1}{2\mu_2} e^{2\mu_2 t} + \frac{2}{A} e^{-At} - \frac{2\omega_1^2}{\omega_b^2 A}\right] \right]} \right]\end{aligned} \tag{76}$$

It is instructive to work out the assymptotic limit of $\kappa(t)$. For a bistable potential of the form $V(q) = aq^4 - bq^2$, the leading order quantum correction is given by $Q(t) = -12\; a\; q(t)\; \langle \delta\hat{q}^2(t) \rangle$. Since the dynamics pertains to the barrier top we have approximately [see Appendix B]

$$G(t) = -\frac{3a}{\omega_b\; \omega_1\; A^2} \left[\hbar^3 \omega_0(\bar{n}_0 + \frac{1}{2})\right]^{1/2} \left[\frac{\omega_1}{\omega_b}\; \sinh 2\omega_b t\; (e^{\mu_1 t} + e^{\mu_2 t}) - 2\cosh^2 \omega_b t\; (e^{\mu_1 t} - e^{\mu_2 t})\right] \tag{77}$$

which may be put in the form

$$G(t) = -\frac{3a}{\omega_b\; \omega_1\; A^2} \left[\hbar^3 \omega_0(\bar{n}_0 + \frac{1}{2})\right]^{1/2} e^{\mu_1 t} \left[\frac{1}{2}\; e^{\ln\omega_1 + 2\omega_b t} - \frac{1}{2}\; e^{\ln\omega_b + 2\omega_b t} - \omega_b\right] \tag{78}$$

in the long time for which $\ln\omega_1 \ll 2\omega_b t$ and $\ln\omega_b \ll 2\omega_b t$. Eq.(78) then gives

$$G(t) = \frac{3\; a}{\omega_b\; \omega_1\; A^2} \left[\hbar^3 \omega_0(\bar{n}_0 + \frac{1}{2})\right]^{1/2} e^{\mu_1 t} \tag{79}$$

Putting Eq.(79) in Eq.(76) and using the limit $t \to \infty$ we obtain the assymptotic expression for the transmission coefficient in the Markovian limit,

$$\kappa(\infty) = \frac{1}{1 + \frac{A\; \hbar\omega_b(\bar{n}_b + \frac{1}{2})}{\mu_1\; \hbar\omega_0(\bar{n}_0 + \frac{1}{2})}} \exp\left[- \frac{18\; a^2\; \hbar^2\; \mu_1\; \omega_0(\bar{n}_0 + \frac{1}{2})}{A^4\; \omega_b^2\; \left(\mu_1\; \omega_0(\bar{n}_0 + \frac{1}{2}) + A\; \omega_b(\bar{n}_b + \frac{1}{2})\right)} \right] \tag{80}$$

In the classical limit as $\hbar \to \infty$, $\hbar\omega_b(\bar{n}_b + \frac{1}{2})$ and $\hbar\omega_0(\bar{n}_0 + \frac{1}{2})$ both goes over to kT; Eq.(80) results in

$$\kappa(\infty) = \left[\frac{1}{1 + \frac{A}{\mu_1}} \right]^{1/2} \tag{81}$$

Since $\mu_1 + \mu_2 = -A$ and $\mu_1 \mu_2 = -\omega_b^2$ the above relation can be put into the following form

$$\kappa(\infty) = \frac{\mu_1}{\omega_b} \tag{82}$$

The classical Markovian coefficient, i.e. , the ratio of the positive unstable root μ_1 to the frequency of the barrier ω_b is therefore reduced to Kramers' prefactor.

C. Non-Markovian friction

We now return to the Eq.(70) and Eq.(71). Corresponding to Eq.(71) we have $\tilde{\gamma}(\mu) = \frac{A\,\alpha}{\mu+\alpha}$ from Eq.(27). $C_v(t)$ is therefore is given by

$$C_v(t) = L^{-1} \left[\mu^2 - \omega_b^2 + \frac{\mu\; A\; \alpha}{\mu + \alpha} \right]^{-1} \tag{83}$$

Following Kohen and Tannor[36] we consider the case when α is small, i.e. , the relevant zeros of the quantity in the parenthesis in Eq.(83) may be written as the solutions of

$$\mu^2 - \omega_b^2 + A\; \alpha = 0 \tag{84}$$

Depending on the relative magnitudes of ω_b^2 and $A\alpha$ it is convenient to discuss two situations $\omega_b^2 - A\alpha > 0$ and $\omega_b^2 - A\;\alpha < 0$ separately.

(i) $\underline{\omega_b^2 - A\;\alpha > 0}$

Here the two roots become $\mu_{1,2} = \pm\sqrt{\omega_b^2 - A\;\alpha}$, with $\mu_1 = -\mu_2$ and $C_v(t)$ is given by

$$C_v(t) = \frac{\sinh \mu_1 t}{\mu_1} \tag{85}$$

Since $\kappa(\omega)\rho(\omega) = \frac{2A}{\pi}\frac{\alpha^2}{\omega^2+\alpha^2}$ we have from Eq.(11) the correlation function as follows;

$$c(t_1 - t_2) = \frac{1}{2} \int_0^\infty d\omega \left(\frac{2A}{\pi} \right) \frac{\alpha^2}{\omega^2 + \alpha^2}\; \hbar\omega \coth\left(\frac{\hbar\omega}{2kT} \right) \cos\omega(t_1 - t_2) \tag{86}$$

Putting Eq.(85) and Eq.(86) in Eq. (28) it is possible to express $A_{11}(t)$ as

$$A_{11}(t) = \frac{A\;\alpha^2\;\hbar \sinh^2 \mu_1 t}{\pi\mu_1^2}\; M - \frac{2\;A\;\alpha^2\;\hbar \sinh \mu_1 t}{\pi\mu_1}\; N - \frac{2\;A\;\alpha^2\;\hbar \cosh \mu_1 t}{\pi}\; O + \frac{A\;\alpha^2\;\hbar}{\pi}\; P \tag{87}$$

where

$$M \;=\; \int_0^\infty \frac{\omega\;\; \coth \frac{\hbar\omega}{2kT}}{(\alpha^2 + \omega^2)\;(\omega^2 + \mu_1^2)}\; d\omega \tag{88}$$

$$N \;=\; \int_0^\infty \frac{\omega^2\;\; \sin\omega t\;\; \coth \frac{\hbar\omega}{2kT}}{(\alpha^2 + \omega^2)\;(\omega^2 + \mu_1^2)^2}\; d\omega \tag{89}$$

$$O \;=\; \int_0^\infty \frac{\omega\;\; \cos\omega t\;\; \coth \frac{\hbar\omega}{2kT}}{(\alpha^2 + \omega^2)\;(\omega^2 + \mu_1^2)^2}\; d\omega \tag{90}$$

$$P \;=\; \int_0^\infty \frac{\omega\;\; \coth \frac{\hbar\omega}{2kT}}{(\alpha^2 + \omega^2)\;(\omega^2 + \mu_1^2)^2}\; d\omega \tag{91}$$

The nonlinear term $G(t)$ in Eq.(69) can be obtained as before by considering the leading order quantum correction as shown in Appendix B for the case $\omega_b^2 - A\alpha > 0$. This is given by

$$G(t) = -\frac{3\ a}{2\ \omega_b\ \mu_1^2\ A\ \alpha} \left[\hbar^3\omega_0 \left(\bar{n}_0 + \frac{1}{2}\right)\right]^{1/2} \left[\mu_1\ \sinh(\mu_1 t) + \frac{A\ \alpha}{\omega_b}\cosh(\mu_1 t)\ \sinh(\frac{2\omega_b}{A}) \right. \\ \left. -\ \omega_b\ \sinh(\frac{2\omega_b}{A})\ \cosh(\mu_1 t - \frac{2\mu_1}{A}) - \mu_1\ \cosh(\frac{2\omega_b}{A})\ \sinh(\mu_1 t - \frac{2\mu_1}{A})\right] \tag{92}$$

Having obtained $C_v(t)$, $A_{11}(t)$ and $G(t)$ from Eq.(85), Eq.(87) and Eq.(92), respectively, we may write down the quantum transmission coefficient using Eq.(69) in the adiabatic regime ($\omega_b^2 > A\alpha$)

$$\kappa(t) = \frac{[\frac{\sinh\mu_1 t}{\mu_1}]}{\left[\frac{\sinh^2\mu_1 t}{\mu_1^2} + \frac{A\alpha^2\hbar}{\pi\hbar\omega_0(\bar{n}_0+\frac{1}{2})}\left[\frac{\sinh^2\mu_1 t}{\mu_1^2}\ M - \frac{2\sinh\mu_1 t}{\mu_1}\ N - 2\cosh\mu_1 t\ O + 2P\right]\right]^{1/2}} \\ \times \exp\left[-\frac{G(t)^2}{2\left\{\hbar\omega_0(\bar{n}_0+\frac{1}{2})\frac{\sinh^2\mu_1 t}{\mu_1^2} + \frac{A\alpha^2\hbar}{\pi}(\frac{\sinh^2\mu_1 t}{\mu_1^2}\ M - \frac{2\sinh\mu_1 t}{\mu_1}\ N - 2\cosh\mu_1 t\ O + 2P)\right\}}\right] \tag{93}$$

In order to check the workability of the above method we first test it against two typical benchmark calculations. To this end we first employ the double-well potential as used earlier in exact numerical calculation of quantum rate coefficient in Ref.[22] with scaled parameters (actual parameters in Table I. of DW1 in Ref.[22]) $E_b = 26.188$, $\omega_b = 1.0$, $\omega_0 = 1.414$ for two different scaled temperatures $kT = 2.617(300K)$ and $kT = 1.744(200K)$. The results for assymtotic transmission coefficient as a function of damping constant from Fig.(9) of Ref.[22] are compared against our analytical expression for the same according to Eq.(93) in Fig.(1). The agreement is excellent at relatively higher temperature i.e. at $kT = 2.617(300K)$. However it is apparent that at lower temperature the analytical results is slightly higher than than exact one. Keeping in view of the fact that the maximum deviation is less than 8 percent and that the analytical quantum correction in Eq.(93) is of lowest order, the result is fairly satisfactory. For a more accurate calculation one would require higher order corrections in $Q(t)$ which can be obtained from numerical solution of the equations in Appendix A and be included in $G(t)$ to be used in Eq.(63). In what follows we also make use of the classical results of Cohen and Tannor[36] for a consistency check of our quantum calculation in the approximate limits as we proceed. We now show the detailed behavior of $\kappa(t)$ as a function of time for different values of temperature T, damping constant A and correlation time $\tau_c(= 1/\alpha)$. To this end we first compare the quantum nature of transmission coefficient as a function of time against its classical counterpart for $A = 50$, $\tau_c = 100$, $kT = 1.0$, $\omega_b = 1.0$, $\omega_0 = \sqrt{2}$ and $a = 0.01$ in Fig.(2). It is apparent that there is a significant increase in quantum values. The variation of temperature has been depicted further in Fig.(3). At higher temperature the quantum coefficient merges into the classical coefficient of Kohen and Tannor[36]. An important new content of the present theory is that it is equipped to deal with zero point fluctuations. Around this teperature the transmission coefficient hardly departs from its maximum value. In Fig.(4) we show the explicit variation of assymptotic transmission coefficient with temperature. While classically $\kappa(t)$ is independent of temperature, quantum nature of the heat bath imparts a temperature dependence which is particularly strong in the low temperature regime. This is one of the most distinctive features of the present calculation.

Fig.(5) shows the two sets of transmission coefficient $\kappa(t)$ as a function of time for different values of dissipation parameters A ranging from 30 to 90 one for quantum and other for the classical. The input parameters are $kT = 1.0$, $\omega_b = 1.0$, $\omega_0 = \sqrt{2}$, $a = 0.01$ and $\tau_c = 100$. It is apparent that there is marginal increase of the corresponding quantum values when compared to the classical transmission coefficient. In Fig.(6) the assymptotic transmission coefficient is plotted as a function of damping constant. The typical behavior in the intermediate to strong dissipation regime is observed which is in complete conformity with the earlier results. Fig.(7) shows an illustrative variation of the time dependent quantum transmission coefficient for several values of correlation time τ_c. With increase in τ_c $\kappa(t)$ increases significantly - a trend which is similar to what is observed in the classical case. With increase in time the transmission coefficient $\kappa(t)$ reaches its plateau value in the Markovian as well as non-adiabatic non-Markovian regime.

(ii) $\underline{\omega_b^2 - A\ \alpha < 0}$

Here from the equation for μ, i.e. , $\mu^2 + (A\ \alpha - \omega_b^2) = 0$ we obtain two purely imaginary roots $\mu_{2,3}$

$$\mu_{2,3} = \pm\ i\tilde{\mu}_2$$

where $\tilde{\mu}_2 = \sqrt{A\alpha - \omega_b^2}$. $C_v(t)$ in this case is given by

$$C_v(t) = \frac{\sin \tilde{\mu}_2 t}{\tilde{\mu}_2} \tag{94}$$

Proceeding as before we arrive at the quantum transmission coefficient in the so called caging regime as follows

$$\begin{aligned}\kappa(t) = & \frac{[\frac{\sin \tilde{\mu}_2 t}{\mu_2}]}{\left[\frac{\sin^2 \tilde{\mu_2} t}{\tilde{\mu_2}^2} + \frac{A\alpha^2\hbar}{\pi\hbar\omega_0(\bar{n}_0+\frac{1}{2})}\left[\frac{\sin^2 \tilde{\mu}_2 t}{\tilde{\mu}_2^2}\ M_1 - \frac{2\sin \mu_2 t}{\tilde{\mu}_2}\ N_1 - 2\cos \tilde{\mu}_2 t\ O_1 + 2P_1\right]\right]^{1/2}} \\ & \times \exp\left[-\frac{G(t)^2}{2\left\{\hbar\omega_0(\bar{n}_0 + \frac{1}{2})\frac{\sin^2 \mu_2 t}{\tilde{\mu}_2^2} + \frac{A\alpha^2\hbar}{\pi}(\frac{\sin^2 \tilde{\mu}_2 t}{\tilde{\mu}_2^2}\ M_1 - \frac{2\sin \tilde{\mu}_2 t}{\tilde{\mu}_2}\ N_1 - 2\cos \tilde{\mu}_2 t\ O_1 + 2P_1)\right\}}\right]\end{aligned} \tag{95}$$

Here $G(t)$ is given by [see Appendix B]

$$\begin{aligned}G(t) = & -\frac{3\ a}{2\ \omega_b\ \tilde{\mu}_2^2\ A\ \alpha}\left[\hbar^3\omega_0\left(\bar{n}_0 + \frac{1}{2}\right)\right]^{1/2}\left[\omega_b\ \sinh\left(\frac{2\omega_b}{A}\right)\ \cos\left(\tilde{\mu}_2 t - \frac{2\ \tilde{\mu}_2}{A}\right)\right. \\ & \left. - \tilde{\mu}_2\ \cosh\left(\frac{2\omega_b}{A}\right)\ \sin\left(\tilde{\mu}_2 t - \frac{2\tilde{\mu}_2}{A}\right) + \tilde{\mu}_2\ \sin\left(\tilde{\mu}_2 t\right) - \frac{A\alpha}{\omega_b}\cos\left(\tilde{\mu}_2 t\right)\ \sinh\left(\frac{2\omega_b}{A}\right)\right]\end{aligned} \tag{96}$$

where

$$M_1 = \int_0^\infty \frac{\omega\ \coth\frac{\hbar\omega}{2kT}}{(\alpha^2 + \omega^2)\ (\omega^2 - \tilde{\mu}_2^2)}\ d\omega \tag{97}$$

$$N_1 = \int_0^\infty \frac{\omega^2\ \sin\omega t\ \coth\frac{\hbar\omega}{2kT}}{(\alpha^2 + \omega^2)\ (\omega^2 - \tilde{\mu}_2^2)^2}\ d\omega \tag{98}$$

$$O_1 = \int_0^\infty \frac{\omega\ \cos\omega t\ \coth\frac{\hbar\omega}{2kT}}{(\alpha^2 + \omega^2)\ (\omega^2 - \tilde{\mu}_2^2)^2}\ d\omega \tag{99}$$

$$P_1 = \int_0^\infty \frac{\omega\ \coth\frac{\hbar\omega}{2kT}}{(\alpha^2 + \omega^2)\ (\omega^2 - \tilde{\mu}_2^2)^2}\ d\omega \tag{100}$$

The behavior of the transmission coefficient is very much similar to that for the classical case as discussed in detail by Kohen and Tannor[36]. In order to allow ourselves a fair comparison with this theory we calculate according to Eq.(95) and the corresponding classical case for the parameters $A = 150$, $\tau_c = 100$, $kT = 1.0$, $\omega_b = 1.0$, $\omega_0 = \sqrt{2}$ and $a = 0.01$. The results are shown in Fig.(8). It is apparent that the oscillating nature persists even in the quantum case although this is accompanied by a loss of amplitude compared to the classical case. In Fig.(9) and Fig.(10) we illustrate the dependence of transmission coefficient with temperature and damping, respectively. Apart from temperature dependence no significant difference from classical behaviour is observed.

IV. CONCLUSION

In this paper we have derived a general time-dependent quantum Kramers'-Grote-Hynes rate constant for a chemical reaction in a condensed medium. This is based on quantum phase space probability distribution functions proposed recently by us to describe quantum Brownian motion in terms of a generalized quantum Langevin equation. We have correlated the time dependence of the transmission coefficient in detail with the variation of dissipation, temperature and correlation time of the noise. Our results can be summarized as follows:

(i) The quantum KGH transmission coefficient Eq.(69), the central result of this paper reduces to to its well known classical limit when $\hbar \to 0$. The expression retains its full validity even in the vacuum limit, i.e. , $T \to 0$.

(ii) We have worked out in detail the specific form of this transmission coefficient in the Markovian as well as in the non-Markovian case. Depending on the dissipation, correlation time and frequency at the barrier top, both adiabatic and non-adiabatic situations have been considered with a comparison with the classical theory of Kohen and Tannor[36].While classical transmission coefficient is independent of temperature its quantum counterpart depends on temperature significantly, particularly in the low temperature regime marked by quantum effects.

(iii) The general expression for quantum KGH transmission coefficient contains quantum corrections to all orders. We have shown that the systematic corrections can be obtained explicitly order by order by simply solving a number of coupled ordinary differential equations.

(iv) The expression for the quantum KGH transmission coefficient is a natural extension of classical theory to quantum domain and provides a unified description of thermally activated process and tunneling.

Before conclusion we now make a few remarks on the present method.

First, since the advent of quantum mechanics several methods of quantization have been in use for description of quantum Brownian motion. Of these, Lagrangian and Hamiltonian formulation have been proposed in the framework of Feynman (path integral) quantization[15,20,45] and been most widely used since early eighties. Dynamical quantization[46,47,48] have been tried with some preliminary success. The present method is based on canonical Heisenberg quantization procedure and has been recently utilized to propose non-Markovian quantum version of Kramers[24,26], Fokker-Planck[25], Smoluchowski[27] and diffusion equations[25]. The main advantage of this approach is that it allows the classical method of solution of equation for probability distribution functions to be applied in the same way as one makes use of flux-over-population method or reactive flux method for calculation of rate coefficients.

Second, since the phase space function formulation of classical reactive flux theory by Kohen and Tannor is particularly useful for visualization of the behaviour of phase space trajectories, a direct extension of this method to the quantum domain as done in the present formulation allows us to achieve a similar objective in terms of c-number trajectories. It is also important to point out that path integral approach also gives rise to several approximations that have a classical flavour[43,44].

Third, an important advantage of this approach is that one not only obtains the asymptotic quantum rate coefficient but also the details of its behaviour at all time *analytically* including its approach towards the steady state. In this sense it is complimentary to the exact numerical work of Ref.[22].

Fourth, although the present method employs system-reservoir oscillator model for evolution of quantum mechanical rate, in the phase space distribution function approach bath co-ordinates do not appear explicitly in the ultimate calculation. One can also avoid multidimensional integration employed in more powerful path integral approach. The present method instead takes care of improvement of quantum corrections successively order by order by solving coupled ordinary differential equations of Appendix (A).

In the view of the above discussions we anticipate that the present approach can readily be adopted to numerical scheme, for example, to that of classical method of Berne and co-workers[49,50], for calculation of time- dependent quantum transmission coefficient beyond linearization over the entire range of friction, noise correlation and temperature, to explain quantum turnover and other interesting features. The work in this direction is in progress.

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APPENDIX A: EVOLUTION EQUATIONS FOR HIGHER-ORDER QUANTUM CORRECTIONS FOR ANHARMONIC POTENTIAL

The equations upto fourth order for quantum corrections (corresponding to the contribution of anharmonicity of the potential) are listed below.
Equations for the second order are:

$$\begin{aligned}
\frac{d}{dt}\langle \delta\hat{q}^2 \rangle &= \langle \delta\hat{q}\delta\hat{p} + \delta\hat{p}\delta\hat{q} \rangle, \\
\frac{d}{dt}\langle \delta\hat{p}^2 \rangle &= -2\Gamma\langle \delta\hat{p}^2 \rangle - V''\langle \delta\hat{q}\delta\hat{p} + \delta\hat{p}\delta\hat{q} \rangle - V'''\langle \delta\hat{q}\delta\hat{p}\delta\hat{q} \rangle, \qquad \text{(A1)} \\
\frac{d}{dt}\langle \delta\hat{q}\delta\hat{p} + \delta\hat{p}\delta\hat{q} \rangle &= -\Gamma\langle \delta\hat{q}\delta\hat{p} + \delta\hat{p}\delta\hat{q} \rangle 2\langle \delta\hat{p}^2 \rangle - 2V''\langle \delta\hat{q}^2 \rangle - V'''\langle \delta\hat{q}^3 \rangle,
\end{aligned}$$

Those for the third order are:

$$\begin{aligned}
\frac{d}{dt}\langle\delta\hat{q}^3\rangle &= 3\langle\delta\hat{q}\delta\hat{p}\delta\hat{q}\rangle,\\
\frac{d}{dt}\langle\delta\hat{p}^3\rangle &= -3\Gamma\langle\delta\hat{p}^3\rangle - 3V''\langle\delta\hat{p}\delta\hat{q}\delta\hat{p}\rangle + V'''\left(\frac{3}{2}\langle\delta\hat{q}^2\rangle\langle\delta\hat{p}^2\rangle - \frac{3}{2}\langle\delta\hat{p}\delta\hat{q}^2\delta\hat{p}\rangle + \hbar^2\right),\\
\frac{d}{dt}\langle\delta\hat{q}\delta\hat{p}\delta\hat{q}\rangle &= -\Gamma\langle\delta\hat{q}\delta\hat{p}\delta\hat{q}\rangle + 2\langle\delta\hat{p}\delta\hat{q}\delta\hat{p}\rangle - V''\langle\delta\hat{q}^3\rangle - \frac{V'''}{2}\left(\langle\delta\hat{q}^4\rangle - \langle\delta\hat{q}^2\rangle^2\right),\\
\frac{d}{dt}\langle\delta\hat{p}\delta\hat{q}\delta\hat{p}\rangle &= -2\Gamma\langle\delta\hat{p}\delta\hat{q}\delta\hat{p}\rangle + \langle\delta\hat{p}^3\rangle - 2V''\langle\delta\hat{q}\delta\hat{p}\delta\hat{q}\rangle\\
&+ \frac{V'''}{2}\left(\langle\delta\hat{q}^2\rangle\langle\delta\hat{q}\delta\hat{p}+\delta\hat{p}\delta\hat{q}\rangle - \langle\delta\hat{q}^3\delta\hat{p}+\delta\hat{p}\delta\hat{q}^3\rangle\right),
\end{aligned}\tag{A2}$$

And lastly, the fourth order equations are:

$$\begin{aligned}
\frac{d}{dt}\langle\delta\hat{q}^4\rangle &= 2\langle\delta\hat{q}^3\delta\hat{p}+\delta\hat{p}\delta\hat{q}^3\rangle,\\
\frac{d}{dt}\langle\delta\hat{p}^4\rangle &= -4\Gamma\langle\delta\hat{p}^4\rangle - 2V''\langle\delta\hat{q}\delta\hat{p}^3+\delta\hat{p}^3\delta\hat{q}\rangle + 2V'''\langle\delta\hat{q}^2\rangle\langle\delta\hat{p}^3\rangle,\\
\frac{d}{dt}\langle\delta\hat{q}^3\delta\hat{p}+\delta\hat{p}\delta\hat{q}^3\rangle &= -\Gamma\langle\delta\hat{q}^3\delta\hat{p}+\delta\hat{p}\delta\hat{q}^3\rangle - 2V''\langle\delta\hat{q}^4\rangle - 3\hbar^2 + 6\langle\delta\hat{p}\delta\hat{q}^2\delta\hat{p}\rangle\\
&+ V'''\langle\delta\hat{q}^2\rangle\langle\delta\hat{q}^3\rangle,\\
\frac{d}{dt}\langle\delta\hat{q}\delta\hat{p}^3+\delta\hat{p}^3\delta\hat{q}\rangle &= -3\Gamma\langle\delta\hat{q}\delta\hat{p}^3+\delta\hat{p}^3\delta\hat{q}\rangle + 2\langle\delta\hat{p}^4\rangle + 3V''(\hbar^2 - 2\langle\delta\hat{p}\delta\hat{q}^2\delta\hat{p}\rangle)\\
&+ 3V'''\langle\delta\hat{q}^2\rangle\langle\delta\hat{p}\delta\hat{q}\delta\hat{p}\rangle,\\
\frac{d}{dt}\langle\delta\hat{p}\delta\hat{q}^2\delta\hat{p}\rangle &= -2\Gamma\langle\delta\hat{p}\delta\hat{q}^2\delta\hat{p}\rangle - V''\langle\delta\hat{q}^3\delta\hat{p}+\delta\hat{p}\delta\hat{q}^3\rangle + \langle\delta\hat{p}^3\delta\hat{q}+\delta\hat{q}\delta\hat{p}^3\rangle\\
&+ V'''\langle\delta\hat{q}^2\rangle\langle\delta\hat{q}\delta\hat{p}\delta\hat{q}\rangle.
\end{aligned}\tag{A3}$$

The derivatives of $V(q)$, i.e., V'' or V''' etc. in the above expressions are functions of q the dynamics of which is given by Eq.(12).

APPENDIX B: CALCULATION OF $G(t)$

It is already been pointed out that $G(t)$ as defined in Eq.(24) describes an interplay of dissipation and nonlinearity in terms of the following convolution integral

$$G(t) = \int_0^t C_v(t-\tau)\ Q(\tau)d\tau \tag{B1}$$

where $Q(t)$ is given by Eq.(15) and the relaxation function $C_v(t)$ refers to Eq.(26) pertaining to the dynamics at the barrier top. When $Q(t)$ is taken in full $G(t)$ contains quantum corrections to all orders and is formally exact. However for practical calculation we evaluate this quantity order by order. Leading order quantum correction in Eq.(15) as given by $Q(t) = -\frac{1}{2}V'''(q)\langle\delta\hat{q}(t)^2\rangle$ for the bistable potential $V(q) = a\ q^4 - b\ q^2$ results in

$$Q(t) = -12\ a\ q(t)\ \langle\delta\hat{q}(t)^2\rangle \tag{B2}$$

Explicit solution of $\langle\delta\hat{q}(t)^2\rangle$ at the barrier top[24,39] at $q = q_0 = 0$ is given by$\langle\delta\hat{q}(t)^2\rangle = \langle\delta\hat{q}^2\rangle_{t=0}\ \cosh 2\omega_b t + \frac{\langle\delta\hat{q}\ \delta\hat{p}+\delta\hat{p}\ \delta\hat{q}\rangle_{t=0}}{2\omega_b}\ \sinh 2\omega_b t$. Furthermore $q(t)$ is known from Eq.(20) upto a leading order so that we have

$$q(t) = p_0\ C_v(t) \tag{B3}$$

Since with minimum uncertainty product state[24,39] we require

$$\langle\delta\hat{q}\ \delta\hat{p}+\delta\hat{p}\ \delta\hat{q}\rangle_{t=0}\ =\ 0 \tag{B4}$$

$$\langle \delta\hat{q}^2 \rangle_{t=0} = \frac{\hbar}{2\omega_b} \tag{B5}$$

and so we have

$$\langle \delta\hat{q}(t)^2 \rangle = \frac{\hbar}{2\omega_b}\ \cosh 2\omega_b t \tag{B6}$$

For an initially thermally distributed p_0 we may write

$$p_0 = \left[\hbar\omega_0(\bar{n}_0 + \frac{1}{2})\right]^{1/2} \tag{B7}$$

With Eq.(B7), Eq.(B6) and Eq.(B3), $Q(t)$ yields

$$Q(t) = -\frac{6\ a\ \hbar^3\omega_0(\bar{n}_0 + \frac{1}{2})}{\omega_b}\ C_v(t)\ \cosh 2\omega_b t \tag{B8}$$

Putting Eq.(B8) in Eq.(B1) we obtain the general expression for $G(t)$ upto the leading order in quantum correction as

$$G(t) = -\frac{6\ a}{\omega_b}\left[\hbar^3\omega_0(\bar{n}_0 + \frac{1}{2})\right]^{1/2}\int_0^t C_v(t-\tau)\ C_v(\tau)\cosh 2\omega_b\tau\ d\tau \tag{B9}$$

The rest of the treatment depends on specific nature of $C_v(t)$.

Case(I) Markovian friction: For this case $C_v(t)$ is given by Eq.(73). Explicit evaluation of the integral in Eq.(B9) results

$$G(t) = -\frac{3\ a}{\omega_1\ \omega_b\ A^2}\left[\hbar^3\omega_0(\bar{n}_0 + \frac{1}{2})\right]^{1/2}\left[\frac{\omega_1}{\omega_b}\ \sinh 2\omega_b t\ (e^{\mu_1 t} + e^{\mu_2 t}) - 2\ \cosh^2\omega_b t\ (e^{\mu_1 t} - (e^{\mu_2 t})\right] \tag{B10}$$

Case(II) non-Markovian friction:

Similarly the evaluation of the integral in Eq.(B9) using $C_v(t)$ from Eq.(85) for the non-adiabatic case $\omega_b^2 - A\alpha > 0$ leads to

$$\begin{aligned} G(t) = -\frac{3\ a}{2\ \omega_b\ \mu_1^2\ A\ \alpha}\left[\hbar^3\omega_0\left(\bar{n}_0 + \frac{1}{2}\right)\right]^{1/2}&\left[\mu_1\ \sinh(\mu_1 t) + \frac{A\ \alpha}{\omega_b}\cosh(\mu_1 t)\ \sinh(\frac{2\omega_b}{A})\right. \\ &\left. - \omega_b\ \sinh(\frac{2\omega_b}{A})\ \cosh(\mu_1 t - \frac{2\mu_1}{A}) - \mu_1\ \cosh(\frac{2\omega_b}{A})\ \sinh(\mu_1 t - \frac{2\mu_1}{A})\right] \end{aligned} \tag{B11}$$

where to avoid divergence we have used a cut off for the integral at time $t = 1/A$. This is a good approximation in view of the fact that quantum correction in Eq.(B11) has been considered to a leading order.

For adiabatic or so called caging regime ($\omega_b^2 - A\alpha < 0$), on the other hand $C_v(t)$ is given by Eq.(94). The corresponding $G(t)$ can be calculated to obtain from Eq.(B9) as

$$\begin{aligned} G(t) = -\frac{3\ a}{2\ \omega_b\ \tilde{\mu}_2^2\ A\ \alpha}&\left[\hbar^3\omega_0\left(\bar{n}_0 + \frac{1}{2}\right)\right]^{1/2}\left[\omega_b\ \sinh\left(\frac{2\omega_b}{A}\right)\ \cosh\left(\tilde{\mu}_2 t - \frac{2\ \tilde{\mu}_2}{A}\right)\right. \\ &\left. - \tilde{\mu}_2\ \cosh\left(\frac{2\omega_b}{A}\right)\ \sinh\left(\tilde{\mu}_2 t - \frac{2\tilde{\mu}_2}{A}\right) + \tilde{\mu}_2\ \sinh(\tilde{\mu}_2 t) - \frac{A\alpha}{\omega_b}\cosh(\tilde{\mu}_2 t)\ \sinh\left(\frac{2\omega_b}{A}\right)\right] \end{aligned} \tag{B12}$$

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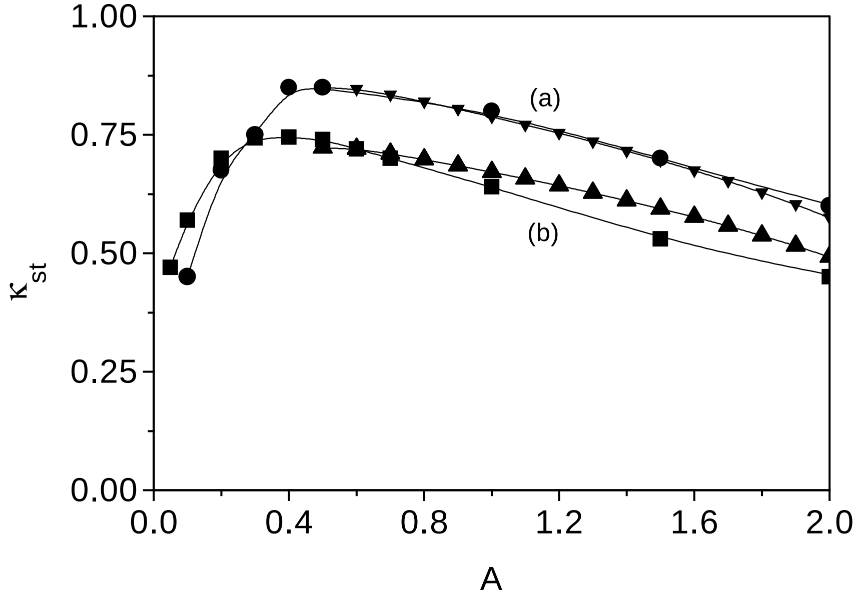

FIG. 1: Asymptotic quantum transmission coefficient κ_{st} is plotted as a function of damping strength (A) at two different temperatures (a) $kT = 2.617(300K)$ and (b) $kT = 1.744(200K)$ for the parameter set mentioned in the text. The numerical results of Fig.9 of Ref.(22) are shown by solid circles and squares and compared to our analytical results (solid triangles) corresponding to Eq.(93).

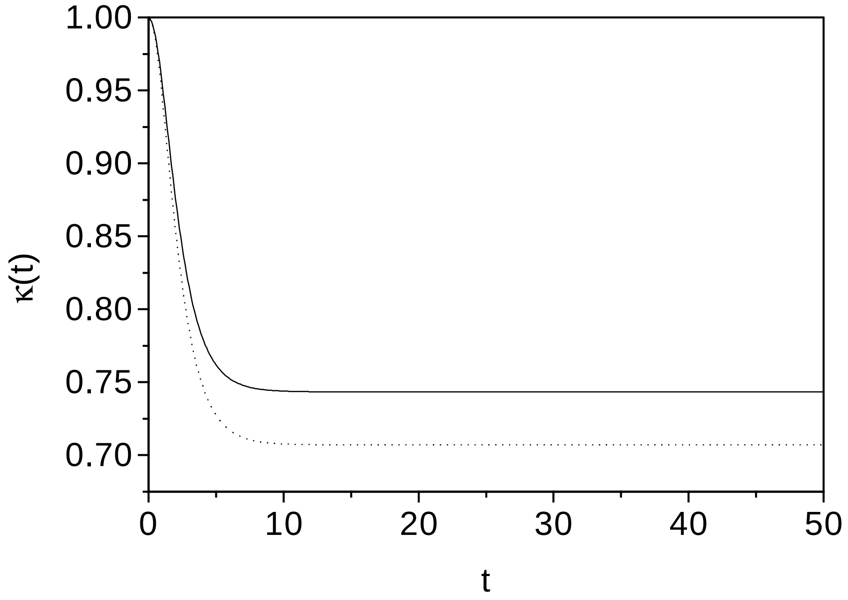

FIG. 2: The quantum (continuous line) transmission coefficient is plotted against time and compared to classical (dotted line) one for the parameter values $A = 50$, $\tau_c = 100$, $kT = 1.0$, $\omega_b = 1.0$, $\omega_0 = \sqrt{2}$, $a = 0.01$.

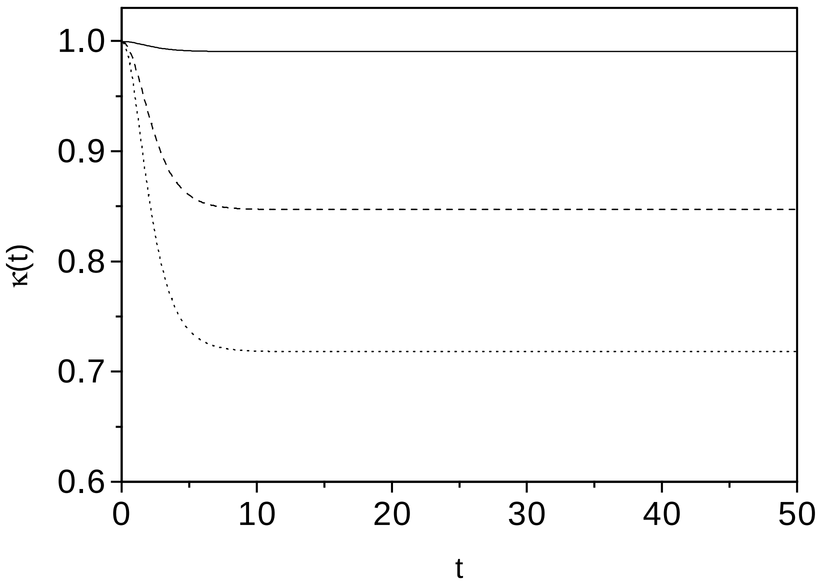

FIG. 3: The quantum transmission coefficient is plotted against time for several values of temperature $kT = 0.0$ (continuous line); $kT = 0.3$ (dashed line); $kT = 25.0$ (dotted line) for $A = 50$, $\tau_c = 100$, $kT = 1.0$, $\omega_b = 1.0$, $\omega_0 = \sqrt{2}$, $a = 0.01$.

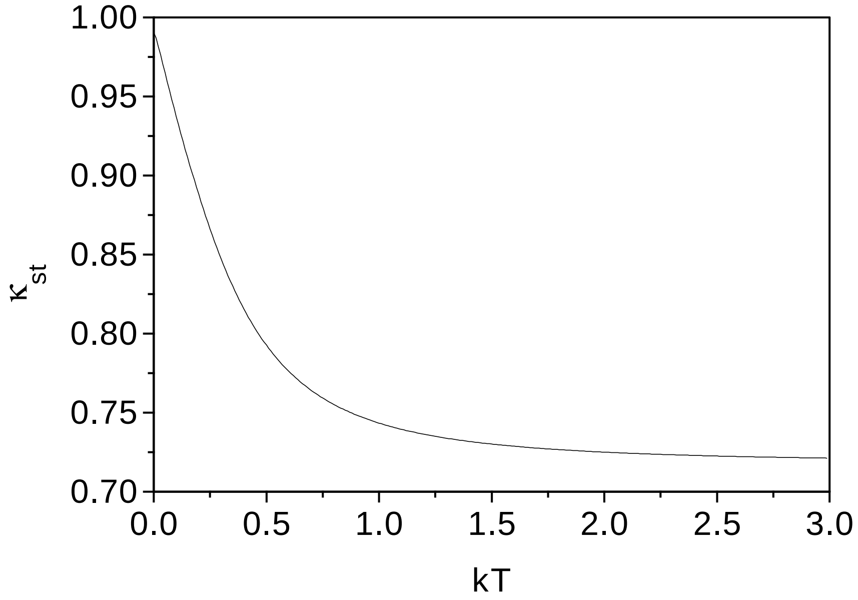

FIG. 4: The assymptotic quantum transmission coefficient κ_{st} is plotted against temperature kT for the set of parameters as in Fig.2.

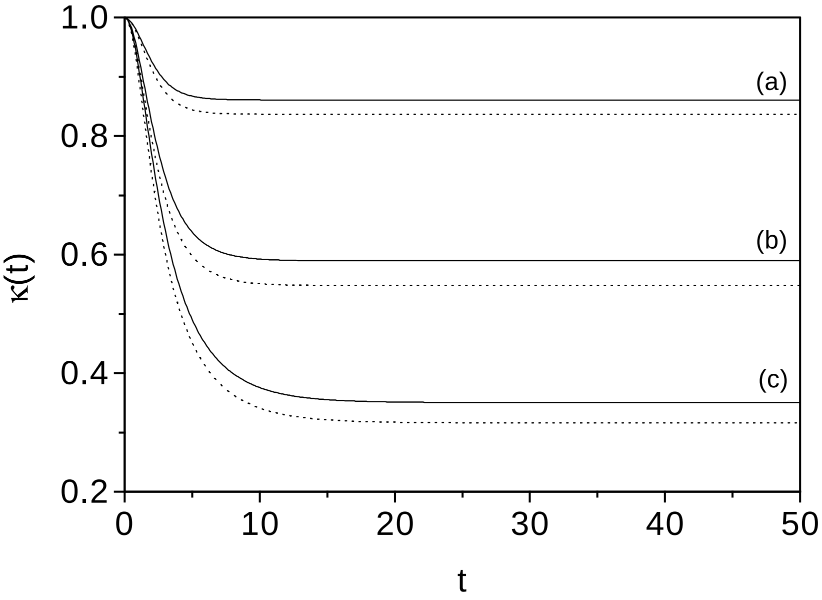

FIG. 5: The quantum (continuous lines) transmission coefficient $\kappa(t)$ is plotted against time for different values of damping constant (a) $A = 30$, (b) $A = 70$, (c) $A = 90$ and compared with classical (dotted lines) ones for the parameters $\tau_c = 100$, $kT = 1.0$, $\omega_b = 1.0$, $\omega_0 = \sqrt{2}$, $a = 0.01$.

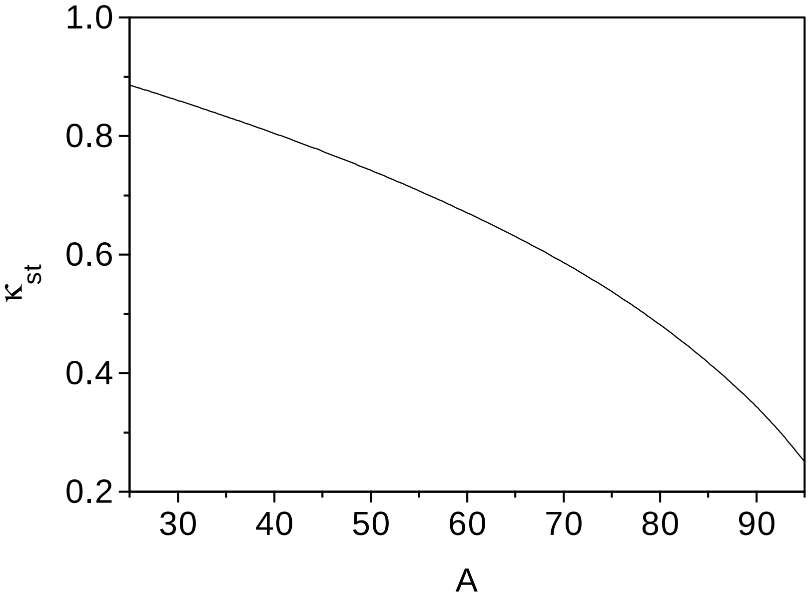

FIG. 6: The assymptotic quantum transmission coefficient $\kappa(t)$ is plotted against damping constant A for the parameter values as in Fig.4.

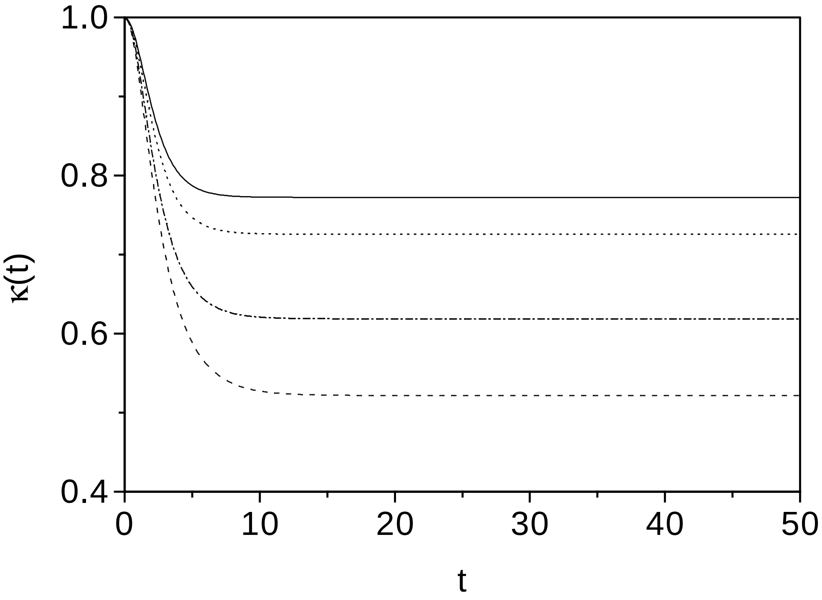

FIG. 7: The quantum transmission coefficient is plotted against time for different values of correlation time, $\tau_c = 65$ (continuous line), $\tau_c = 75$ (dotted line), $\tau_c = 95$ (dashed and dotted line), $\tau_c = 110$ (dashed line) for other parameters as in Fig.4.

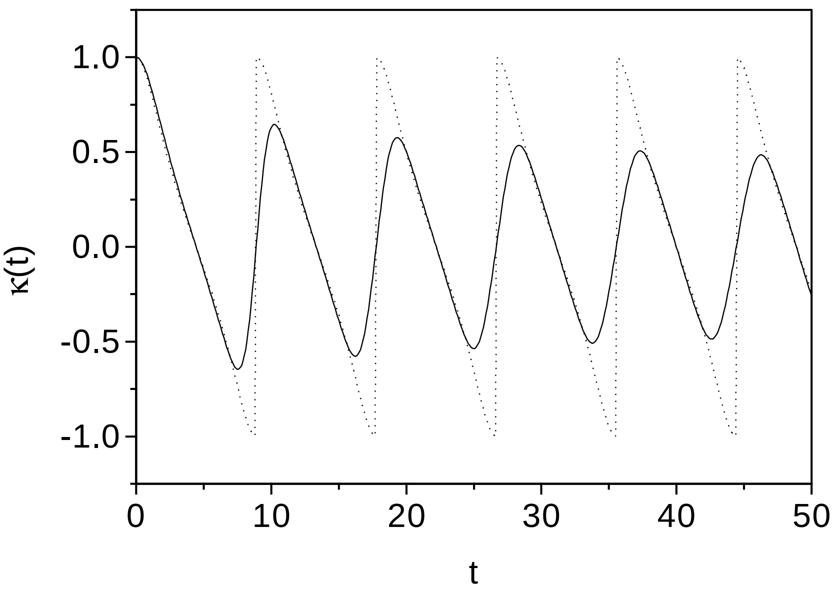

FIG. 8: The quantum (continuous line) transmission coefficient is plotted against time and compared with classical (dotted line) one for the set of parameters $A = 150$, $\tau_c = 100$, $kT = 1.0$, $\omega_b = 1.0$, $\omega_0 = \sqrt{2}$, $a = 0.01$ (in the caging regime).

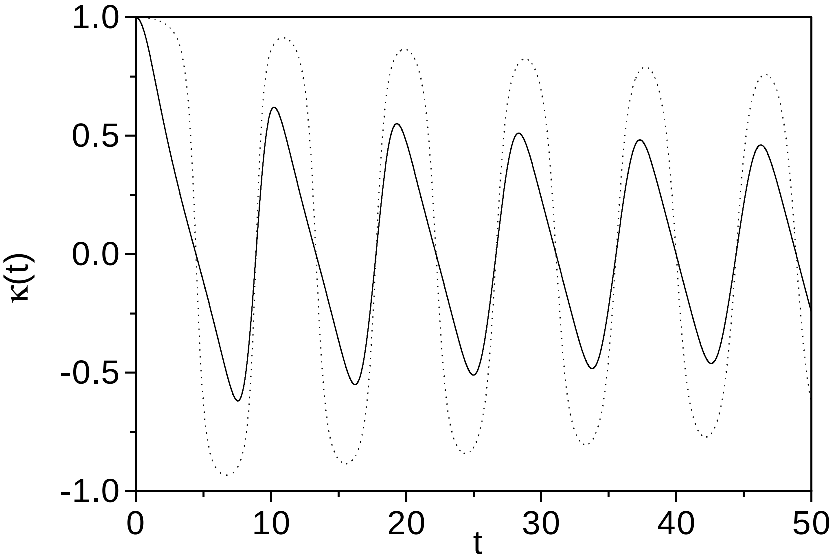

FIG. 9: Same as in Fig.7 but for $kT = 0.0$ (dotted line), and $kT = 25.0$ (continuous line).

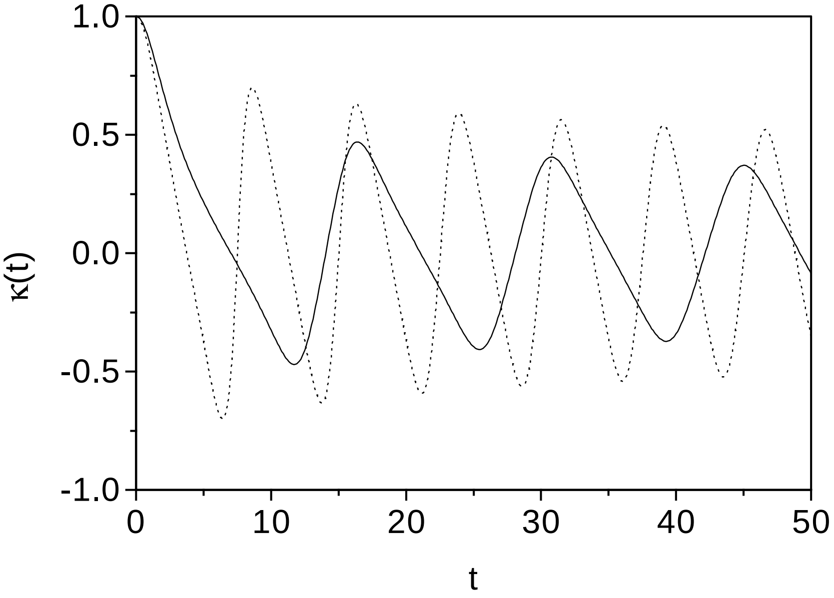

FIG. 10: Same as in Fig.7 but for $A = 120$ (continuous line) and $A = 170$ (dotted line).