A simple semiclassical approach to Kramers' problem

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Abstract

We show that Wigner-Leggett-Caldeira equation for Wigner phase space distribution function which describes the quantum Brownian motion of a particle in a force field in a high temerature, Ohmic environment can be identified as a semiclassical version of Kramers' equation. Based on an expansion in powers of $\hbar$ we solve this equation to calculate the semiclassical correction to Kramers' rate.

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I. INTRODUCTION

The recent two decades have witnessed a phenomenal development of the theory of noise induced escape from metastable states. The escape is governed by Brownian motion in addition to the characteristic dynamical motion of the system in presence of the potential field, $V(x)$, Brownian motion being driven by thermal forces which, in turn, are associated with the dissipation γ through the fluctuation-dissipation theorem at finite temperature T. The problem[1] has been addressed by a large number of workers both from classical and quantum mechanical point of view at various levels of description under a variety of reasonable approximations in the weak, strong and intermediate damping limits. The rate theory thus constitutes a well-developed body of literature by now[2,3].

Although a number of interesting approaches to quantum theory of dissipative rate processes based on dynamical semigroup method for evolution of density operator were proposed[4,5] in seventies to treat the quantum and nonlinear optical phenomena with considerable success, the method could not gain good ground in the theory of rate processes due to the fact that it is based on weak system-reservoir coupling ($\gamma \ll \omega$). The method which got major appreciation afterwards in eighties and nineties in the wide community of physicists and chemists is the real time functional integrals. This method has shown to be most effective in treating quantum transition states[6–8], dissipative coherence quantum effects as well as the incoherent quantum tunneling processes[2,3,9–11]. The latter processes being more relevant in the present context. Notwithstanding its phenomenal success, it may, however, be noted that compared to classical Kramers' theory the method of functional integrals for calculation of rate rests on a fundamentally different footing. While the classical theory is based on the differential equation for evolution of probability distribution function of a particle executing Brownian motion in a force field, path integral methods rely on the evaluation of quantum partition function of the system interacting with a bath of harmonic oscillators with a characteristic distribution of frequencies[11]. The question is whether there is any natural extension of the classical method to the quantum domain or in other words

what is the analogue of Kramers' equation in the quantum regime. For this one has to look for an equation for evolution of a quantum probability distribution function of a particle in a force field driven by quantum Brownian motion. Unfortunately the theory of quantum Brownian motion in terms of phase space probability function[11] is far from complete. Under restricted conditions one may use either weak damping limit ($\gamma \ll \omega$) or take resort to semiclassical procedure ($k_BT \gg \hbar\omega$) and arbitrary damping. Thus, strictly speaking, to the best of our knowledge, there exist no full quantum analogue of Kramers' equation valid for arbitrary damping and temperature.

Our aim in this paper is two-fold :

i) Although there exists no full quantum analogue of Kramers' equation, we enquire whether there is any semiclassical Kramers' equation. We show that the Wigner-Leggett-Caldeira [WLC] equation [see Eq.(2.3)] for Wigner probability phase space function which describes the quantum Brownian motion of the particle in a force field in a high temperature Ohmic environment may be interpreted as a semiclassical Kramers' equation. WLC equation reduces to classical Kramers' equation in the limit $\hbar \to 0$.

ii) While the existing methods of calculation of quantum Kramers' rate are based on path integral technique, we solve the semiclassical Kramers' equation for barrier crossing dynamics as a boundary value problem to calculate the leading order ($\hbar^2$-order) quantum correction to classical rate. WLC equation had been used earlier in connection with quantum decoherence[12] and other problems[13,14]. To the best of our knowledge the implementation of a differential equation-based approach for the calculation of quantum Kramers' rate like the present one had not been tried upto date.

The outlay of the paper is as follows. In Sec. II we discuss the quantum dynamics of a dissipative system and show that a WLC equation for Wigner probability density function may serve as a good description for noise-induced escape rate in the semiclassical regime. In Sec. III elementary formulas are summarized. We apply the appropriate boundary conditions and make use of an $\hbar$-expansion to solve the differential equation for stationary probability function in Sec. IV. In Sec. V we calculate the steady state flux over the barrier, population

inside the well and the escape rate and show that the quantum contribution appears in the order $\hbar^2$. The paper is concluded in Sec. VI.

II. QUANTUM DYNAMICS OF A DISSIPATIVE SYSTEM

We consider a dynamical system characterized by a potential $V(x)$ coupled to an environment. The latter is modeled as a set of harmonic oscillators with frequencies $\{\Omega_j\}$. Evolution of such an open quantum system has been studied over the last several decades under a variety of reasonable assumptions[2–5,11]. Specifically interesting is the semiclassical limit of a high temperature Ohmic environment[11]. The dissipative time evolution of the Wigner distribution function $W(x,v,t)$ for the system with unit mass ($m=1$) for arbitrarily strong damping in this case can be described by[11]

$$\left(\frac{\partial W}{\partial t}\right)_{dissipative} = 2\gamma\frac{\partial(vW)}{\partial v} + D\frac{\partial^2 W}{\partial v^2} \quad , \tag{2.1}$$

where γ and D are the dissipation constant and the diffusion coefficient, respectively. The microscopic structure of γ is given in Ref.[11]. x and v are c-number co-ordinate and velocity variables. The first term in Eq.(2.1) is a direct consequence of the existence of γ-dependent term in the imaginary part of the exponent in the expression for the propagator for the density operator in the Feynman-Vernon theory and has been shown to be responsible for appearance of a damping force in the classical equation of motion for the Brownian particle to ensure quantum-classical correspondence. γ and D are related by the fluctuation-dissipation relation, $D = \gamma\hbar\omega\coth\frac{\hbar\omega}{2k_BT}$ (in the semiclassical limit $D \to 2\gamma k_BT$ and $W(x,v,t)$ reduces to classical phase space distribution function). ω is the renormalized linear frequency of the nonlinear system. The quantum dynamics of the bare system on the other hand is governed by the celebrated Wigner equation[15] as given by

$$\left(\frac{\partial W}{\partial t}\right)_{dynamical} = -v\frac{\partial W}{\partial x} + \frac{\partial V}{\partial x}\frac{\partial W}{\partial v} + \sum_{n\geq 1}\frac{\hbar^{2n}(-1)^n}{2^{2n}(2n+1)!}\frac{\partial^{2n+1}V}{\partial x^{2n+1}}\frac{\partial^{2n+1}W}{\partial v^{2n+1}} \quad . \tag{2.2}$$

The above c-number description (2.2) is equivalent to full Schrödinger equation. The quantum correction to classical Liouville motion is contained in the $\hbar$-containing terms in

the sum. We emphasize here that while (2.1) is a *semiclassical Brownian dynamics* due to the coupling of an Ohmic environment to the system, Eq (2.2) takes into account of the full *quantum nature* of the system. The overall dynamics is then given by

$$\left(\frac{\partial W}{\partial t}\right) = \left(\frac{\partial W}{\partial t}\right)_{dynamical} + \left(\frac{\partial W}{\partial t}\right)_{dissipative} \quad ,$$

or

$$\frac{\partial W}{\partial t} = -v\frac{\partial W}{\partial x} + \frac{\partial V}{\partial x}\frac{\partial W}{\partial v} + \sum_{n\geq 1} \frac{\hbar^{2n}(-1)^n}{2^{2n}(2n+1)!}\frac{\partial^{2n+1}V}{\partial x^{2n+1}}\frac{\partial^{2n+1}W}{\partial v^{2n+1}} + 2\gamma\frac{\partial(vW)}{\partial v} + D\frac{\partial^2 W}{\partial v^2} \quad . \quad (2.3)$$

The WLC equation, (2.3) is the starting point of our further analysis. Before proceeding further several points are to be noted :

First, strictly speaking γ and D terms in Eq.(2.1) are valid in (2.3) if the system operators pertain to a harmonic oscillator. When the system is nonlinear, as in the present study (and in the overwhelming majority of the cases in quantum and nonlinear optics), the usual practice is to assume that the dissipative terms remain unaffected by the Wigner higher derivative terms in Eq. (2.2). The validity of this assumption was examined earlier by Haake et. al.[16] and also by us[17]. It is now well-known that the assumption is quite satisfactory in semiclassical limit and when nonlinearity is not too strong. Since the calculation of barrier crossing dynamics needs the linearization of the potential at the barrier top as an essential step, the nonlinearity of the potential $V(x)$ must be weak. This assumption is essential for validity of Eq.(2.3). We also mention here that weakness of nonlinearity is essential for the linearized description of the potential near the extrema in almost all theories including path integral techniques upto date[18–21].

Second, the system-reservoir dynamics as governed by Eq.(2.3) or (2.1) is based on Markov approximation which implies that the underlying stochastic process due to reservoir is Markovian by construction as in classical theory. However in deriving Eq.(2.3) or (2.1) the system-reservoir coupling is assumed to be arbitrary[11]. Thus Eq.(2.3) is applicable to both in the strong and weak damping limit. Since we are considering here the spatial-diffusion limited rate we restrict ourselves from intermediate to strong damping range.

Eq.(2.3) has been used earlier in several occasions. For example, Zurek and Paz[12] have studied some interesting aspects of quantum-classical correspondence in relation to decoherence. Based on this equation a theory of quantum noise in classically chaotic dissipative systems has been formulated[13,14]. The primary reason for choosing Eq.(2.3) as our starting point is that it reaches the correct classical limit, i.e., the classical Kramers' equation when $\hbar \to 0$ and D becomes a thermal diffusion coefficient in the high temperature limit and $W(x, v, t)$ reduces to classical probability distribution function in phase space. Thus the WLC equation (2.3) may be interpreted as a semiclassical Kramers' equation.

Our object here is to search for a semiclassical solution in powers of $\hbar$ for the WLC equation (2.3) under appropriate boundary conditions and calculation of the barrier crossing rate in the intermediate to strong damping regime.

III. THE MODEL, THE STATIONARY FLUX AND THE WELL POPULATION

We now consider a particle of unit mass moving in a cubic potential $V(x)$ of the form

$$V(x) = -\frac{1}{3}Ax^3 + Bx^2 \quad , \tag{3.1}$$

where x now corresponds to the reaction co-ordinate and its values at the extrema of the potential at $x = 0$ and $x = x_0$ denote the reactant and the transition state, respectively. In this model all the remaining relevant degrees of freedom of the system and the environment constitute a heat bath at a finite temperature T. Eq.(2.3) with Eq.(3.1) provides a complete description of the stochastic process in terms of Wigner probability density function of the c-number variables x, v.

One of the decisive advantage of using Wigner's phase space language is that it offers an excellent opportunity to extend the classical formulae to the quantum domain when one replaces the classical probability functions by the Wigner density functions. Thus the original reasoning of Farkas and Kramers[1,2] can be followed in the present problem to determine the steady state escape rate from the well by considering a steady state situation in which

a steady state probability current is maintained between the source and the sink, the latter being situated beyond the transition state. The standard expression for escape rate in terms of flux over the population is thus given by

$$k = \frac{j}{n_a} \tag{3.2}$$

where

$$j = \int_{-\infty}^{+\infty} dv\ v\ W(x_0, v) \tag{3.3}$$

and

$$n_a = \int_{left\ well} \int dx\ dv\ W(x, v) \tag{3.4}$$

and $W(x, v)$ is the steady state Wigner probability density function.

IV. THE STEADY STATE SEMICLASSICAL DESCRIPTION : BOUNDARY CONDITIONS

The search for a semiclassical probability distribution function $W(x, v)$ for Eq.(2.3) essentially rests on developing $W(x, v)$ in a power series of $\hbar$. Thus we write[15]

$$W(x, v) = e^{-\beta\epsilon} \left[\rho_0(x, v) + \hbar\ \rho_1(x, v) + \hbar^2\ \rho_2(x, v) + \ldots\right] \tag{4.1}$$

where $\beta = 1/k_B T$ and $\epsilon = \frac{1}{2}v^2 + V(x)$. As pointed out by Wigner[15], ρ_k will not involve higher derivatives of V than k-th, nor higher powers of v than k-th. This is relevant for the explicit form of $V(x)$ as given by Eq.(3.1) in the present case and for calculation of higher terms in Eq.(4.1) in a simpler way.

By inserting (4.1) in Eq.(2.3) and equating the coefficients of different powers of $\hbar$ in the usual way and putting $\frac{\partial W}{\partial t} = 0$ we obtain the following equations,

$$D\frac{\partial^2 \rho_0}{\partial v^2} + \left\{\frac{\partial V}{\partial x} - 2\gamma v\right\} \frac{\partial \rho_0}{\partial v} - v\frac{\partial \rho_0}{\partial x} = 0 \tag{4.2a}$$

$$D\frac{\partial^2\rho_1}{\partial v^2}+\left\{\frac{\partial V}{\partial x}-2\gamma v\right\}\frac{\partial\rho_1}{\partial v}-v\frac{\partial\rho_1}{\partial x}=0 \tag{4.2b}$$

$$D\frac{\partial^2\rho_2}{\partial v^2}+\left\{\frac{\partial V}{\partial x}-2\gamma v\right\}\frac{\partial\rho_2}{\partial v}-v\frac{\partial\rho_2}{\partial x}=\frac{1}{4!}\frac{\partial^3 V}{\partial x^3}\left[\left\{\frac{12\gamma^2}{D^2}v-\frac{8\gamma^3}{D^3}v^3\right\}\rho_0 + \left\{\frac{12\gamma^2}{D^2}v^2-\frac{6\gamma}{D}\right\}\frac{\partial\rho_0}{\partial v}-\frac{6\gamma}{D}v\frac{\partial^2\rho_0}{\partial v^2}+\frac{\partial^3\rho_0}{\partial v^3}\right] \tag{4.2c}$$

and so on.

We note that the Eqs.(4.2a),(4.2b) are homogenous partial differential equations while (4.2c) is an inhomogenous one. The inhomogenous contribution begins to appear from ρ_2-term which is associated as a coefficient of $\hbar^2$ in the expansion (4.1). The leading order quantum contribution (since ρ_1 does not contribute[15]) through ρ_2 involves only cubic derivative of the potential in (4.2c). The other derivatives of any arbitrary potential $V(x)$ contribute to the terms containing higher powers of $\hbar$ (e.g., $\hbar^4$, $\hbar^6$ etc.). Thus the leading order nonlinearity that affects the dynamics at the semiclassical level must at best be cubic one.

Eq.(4.2a) is the evolution of familiar *dynamical* contribution from classical Kramers' equation. The leading order quantum correction starts at $\hbar^2$[15]. Thus W has the form

$$W(x,v)=e^{-\beta\epsilon}\left[\,\rho_0(x,v)+\hbar^2\rho_2(x,v)+\ldots\,\right] \tag{4.3}$$

where ρ_0 and ρ_2 are the solutions of the equations (4.2a) and (4.2c) respectively.

To obtain the steady state probability density $W(x,v)$ several requirements[1] must be fulfilled:

(i) Near the bottom of the well all the particles are thermalized and are in a state of thermal equilibrium. In the classical case the probability density is given by the Boltzmann distribution. In the present semiclassical case the corresponding distribution function contains an appropriate Wigner quantum corrections of $\hbar^2$ order to Boltzmann distribution. According to Wigner the semiclassical equilibrium distribution is given by

$$W_{BW}(x,v)=e^{-\beta\epsilon}+\hbar f_1+\hbar^2 f_2+\ldots \tag{4.4}$$

which is to be obtained as a solution of Eq.(2.2).

Following Wigner[15] one can easily show that

$$f_1 = 0 \tag{4.5}$$

and

$$f_2 = 4\pi^2\, e^{-\beta\epsilon}\left[-\frac{\beta^2}{8}\frac{\partial^2 V}{\partial x^2} + \frac{\beta^3}{28}\left(\frac{\partial V}{\partial x}\right)^2 + \frac{\beta^3 v^2}{24}\frac{\partial^2 V}{\partial x^2}\right] \tag{4.6}$$

We emphasize the distinguishing feature of the two expansions (4.3) and (4.4). While (4.4) refers to an *equilibrium* thermal Boltzmann-Wigner distribution, (4.3) denotes a *steady state* Wigner-Kramers distribution which takes into account of semiclassical Brownian dynamics. (4.1) may be viewed as a generalization of Kramers' ansatz in the quantum mechanical context.

We make use of the solutions (4.4-4.5) near the bottom of the well. We thus impose the following condition on $W(x,v)$ of (4.3) as

$$W(x,v) \longrightarrow W_{BW}(x,v) \quad \text{as } x \approx 0 \quad \text{and all } v \ . \tag{4.7a}$$

This, in turn, implies $\rho_0(x,v) \to 1$ and $\rho_2(x,v) \to e^{+\beta\epsilon} f_2$.

(ii) On the other hand beyond the transition state, i.e., $x = x_0$ all the particles are removed by the sink, or,

$$W(x,v) \approx 0 \quad \text{as } x > x_0 \quad \text{for all } v \ . \tag{4.7b}$$

Having specified the boundary conditions (4.7a,4.7b) for Wigner distribution function $W(x,v)$ we now elucidate the dynamics near the barrier at $x = x_0$. Near this point we assume the usual linearized potential (with frequency ω_b),

$$V(x) = E_0 - \frac{1}{2}\omega_b^2 (x - x_0)^2 \tag{4.8}$$

where E_0 is the barrier height and

$$\omega_b^2 = -V''(x_0) > 0 \ . \tag{4.9}$$

The probability distribution function $W(x,v)$ is determined by $\rho_0(x,v)$ and $\rho_2(x,v)$ which obey the following stationary equations around the barrier ;

$$D\frac{\partial^2\rho_0}{\partial v^2}+\left\{-\omega_b^2(x-x_0)-2\gamma v\right\}\frac{\partial\rho_0}{\partial v}-v\frac{\partial\rho_0}{\partial x}=0 \tag{4.10}$$

and

$$\begin{aligned} &D\frac{\partial^2\rho_2}{\partial v^2}+\left\{-\omega_b^2(x-x_0)-2\gamma v\right\}\frac{\partial\rho_2}{\partial v}-v\frac{\partial\rho_2}{\partial x} \\ &=-\frac{1}{12}\,A\,\left[\left\{\,\frac{12\gamma^2}{D^2}v-\frac{8\gamma^3}{D^3}v^3\,\right\}\rho_0+\left(\,\frac{12\gamma^2}{D}v-6\gamma\,\right)\frac{\partial\rho_0}{\partial v}-6\gamma v\frac{\partial^2\rho_0}{\partial v^2}+D\frac{\partial^3\rho_0}{\partial v^3}\,\right] \end{aligned} \tag{4.11}$$

The inhomogenous term in Eq.(4.11) requires the solution $\rho_0(x,v)$, which can be obtained by solving (4.10) directly using Kramers' method[1,2] and is given by

$$\rho_0(u)=C_0\int_0^u\exp\left\{-\frac{\lambda}{2D}z^2\right\}\,dz+C_0' \tag{4.12}$$

where C_0 and C_0' are constants to be determined. Here

$$u=v+a(x-x_0) \tag{4.13}$$

where a is a solution of $a^2+2\gamma a-\omega_b^2=0$ and $\lambda=-(2\gamma+a)$. The relevant root of a which makes $\lambda>0$ is $a_-=-\gamma-\sqrt{\gamma^2+\omega_b^2}$), so that $\lambda=-\gamma+\sqrt{\gamma^2+\omega_b^2}$. The requirement that

$$\rho_0\longrightarrow 0\quad\text{as}\;\;x\;\rightarrow\;\infty \tag{4.14}$$

implies $C_0'=C_0\sqrt{\frac{\pi D}{2\lambda}}$. Thus

$$\rho_0(u)=C_0\left[\,\sqrt{\frac{\pi D}{2\lambda}}+\int_0^u\exp\left\{-\frac{\lambda}{D}z^2\right\}\,dz\,\right] \tag{4.15}$$

Eq.(4.15) is essentially the Kramers' solution which we now use to determine the inhomogenous terms in equation for ρ_2 (Eq.(4.11)). Three pertinent points are to noted here. Since we are working in the semiclassical limit $k_BT>\hbar\omega$, we keep the terms upto the $\mathcal{O}\left[\left(\frac{1}{k_BT}\right)^2\right]$ in the inhomogenous part. Second, we take into account of the Wigner's remark[15] on quantum contribution contained in ρ_2 term. The term has been "interpreted as meaning that a quick variation of the probability function with co-ordinates is unlikely, as it would mean

a quick variation, a short wavelength, in the wave functions. This however would have the consequence of high kinetic energy". The finite range of co-ordinates therefore ranges over $\sim \hbar/\overline{v}$ where $\overline{v}$ is mean momentum $\sim (k_B T)^{1/2}$. Thirdly, we also note that the leading order nonlinearity enters through the cubic derivative of the potential (3.1) in the inhomogenous term.

Based on these consideration we are now led to the following equation for ρ_2 :

$$\frac{d^2\rho_2}{du^2} + \frac{\lambda}{D} u \frac{d\rho_2}{du} = (-M_1 - M_2 u - M_3 u^2) \exp\left(-\frac{\lambda u^2}{2D}\right) \quad , \tag{4.16}$$

where the transformation of derivatives has been carried using the change of variables through the linear combination of x and v as expressed in (4.13). M_1, M_2 and M_3 are given by

$$M_1 = A\, C_0 \left\{ \frac{\gamma^2}{D^3}(k_B T) - \frac{\gamma}{2D^2} - \frac{\lambda}{12 D^2} \right\} \quad , \tag{4.17a}$$

$$M_2 = A\, C_0\, \frac{\gamma\lambda}{2D^3}(k_B T)^{1/2} \tag{4.17b}$$

$$\text{and} \quad M_3 = A\, C_0\, \frac{\lambda^2}{12 D^3} \tag{4.17c}$$

It may be noted that all the three terms in the source term of Eq.(4.16) are within $(1/k_B T)^2$ order (This may be checked by noting that u behaves as v near $x = x_0$ and $\overline{v} \sim (k_B T)^{1/2}$ as argued earlier).

The general solution of Eq.(4.16) subject to boundary condition,

$$\rho_2 \longrightarrow 0 \quad \text{as} \quad x \to \infty \tag{4.18}$$

is given by

$$\begin{aligned} \rho_2(u) = & \left[\frac{M_1 D}{\lambda} + \frac{M_2 D}{2\lambda}\, u + \frac{M_3 D}{3\lambda}\, u^2 + \frac{2}{3}\frac{M_3 D^2}{\lambda^2} \right] \exp\left(-\frac{\lambda u^2}{2D}\right) \\ & + \left(C_2 - \frac{M_2 D}{2\lambda}\right) \int_0^u \exp\left(-\frac{\lambda z^2}{2D}\right)\, dz + \sqrt{\frac{\pi D}{2\lambda}} \left(C_2 - \frac{M_2 D}{2\lambda}\right) \quad , \end{aligned} \tag{4.19}$$

where C_2 is an integration constant to be determined and $u = v - |a_-|(x - x_0)$ with $|a_-| = \gamma + \sqrt{\gamma^2 + \omega_b^2}$. Thus upto $\hbar^2$ our distribution function (4.3) becomes

$$W(u) = e^{-\beta\epsilon} \left[\rho_0(u) + \hbar^2 \rho_2(u) \right] \ , \tag{4.20}$$

where $\rho_0(u)$ and $\rho_2(u)$ are given by (4.15) and (4.19), respectively.

To determine the two unknown constants C_0 and C_2 we now employ the boundary condition (4.7a), which implies that the probability density function $W(u)$ of (4.20) must coincide with the thermal Boltzmann-Wigner distribution $W_{BW}(x,v)$ of Eq.(4.4) near $x = 0$.

Thus we have from (4.20) [i.e., from (4.15) and (4.19)]

$$W(x,v) \overset{x\to-\infty}{\longrightarrow} e^{-\beta\epsilon} \left[C_0 \sqrt{\frac{2\pi D}{\lambda}} + \hbar^2 \left(C_2 - \frac{M_2 D}{2\lambda} \right) \sqrt{\frac{2\pi D}{\lambda}} \right] \tag{4.21}$$

on the other hand $W_{BW}(x,v)$ of (4.4) [with (4.5) and (4.6)] near the bottom of the well at $x = 0$ where the linearized potential

$$V(x) = \frac{1}{2}\omega_0^2 x^2 \tag{4.22}$$

may be used, behaves as the Boltzmann-Wigner distribution of the particles at thermal equilibrium ;

$$W_{BW}(x,v) \overset{\text{Near } x=0}{\longrightarrow} e^{-\beta\epsilon} \left[1 - \frac{1}{3}\hbar^2 \pi^2 \beta^2 \omega_0^2 \right] \ . \tag{4.23}$$

Matching of (4.21) and (4.23) suggests that

$$C_0 = \sqrt{\frac{\lambda}{2\pi D}} \tag{4.24a}$$

and

$$\left(\frac{M_2 D}{2\lambda} - C_2 \right) = \frac{1}{3} \sqrt{\frac{\lambda}{2\pi D}} \, \pi^2 \beta^2 \omega_0^2 \ . \tag{4.24b}$$

The boundary condition (4.7a) therefore uniquely determines the probability distribution function (4.20) where ρ_0 and ρ_2 are given by (4.15) and (4.19) and C_0 and C_2 by (4.24a,4.24b) respectively. The resultant unnormalized expression is as follows:

$$\begin{aligned} W(x,v) = e^{-\beta\epsilon} \Bigg[& \sqrt{\frac{\lambda}{2\pi D}} \left\{ \sqrt{\frac{\pi D}{2\lambda}} + \int_0^u \exp\left(-\frac{\lambda}{D} z^2 \right) \, dz \right\} \\ & + \hbar^2 \left\{ \exp\left(-\frac{\lambda}{D} u^2 \right) \left(\frac{M_1 D}{\lambda} + \frac{M_2 D}{2\lambda} \, u + \frac{M_3 D}{3\lambda} \, u^2 + \frac{2}{3} \frac{M_3 D^2}{\lambda^2} \right) \right. \\ & \left. - \frac{1}{3} \sqrt{\frac{\lambda}{2\pi D}} \, \pi^2 \, \beta^2 \, \omega_0^2 \int_0^u \exp\left(-\frac{\lambda}{2D} z^2 \right) \, dz \, - \frac{1}{6} \pi^2 \, \beta^2 \, \omega_0^2 \right\} \Bigg] \end{aligned} \tag{4.25}$$

with $u = v - |a_-|(x - x_0)$.

V. THE ESCAPE RATE

In order to determine the semiclassical rate of escape we now make use of the flux-over-population formula (3.2). To this end we obtain the well population from Eqs.(3.4) and (4.25), assuming the linearized potential $V(x) = \frac{1}{2}\omega_0^2 x^2$ near the bottom of the well at $x = 0$.

$$n_a = \frac{2\pi}{\omega_0 \beta} \left[1 - \frac{1}{3}\hbar^2 \pi^2 \beta^2 \omega_0^2 \right] \quad . \tag{5.1}$$

The probability current (3.3) becomes

$$j = e^{-\beta E_0} \left[\sqrt{\frac{\lambda}{2\pi D}} \, \frac{1}{\beta} \, \sqrt{\frac{\pi}{\frac{\beta}{2} + \frac{\lambda}{2D}}} \right.$$
$$\left. + \hbar^2 \left\{ \frac{M_2 D}{2\lambda} \, \frac{1}{\frac{\lambda}{D} + \beta} \, \sqrt{\frac{\pi}{\frac{\beta}{2} + \frac{\lambda}{2D}}} - \frac{1}{3} \sqrt{\frac{\lambda}{2\pi D}} \, \pi^2 \, \omega_0^2 \, \beta^2 \, \frac{1}{\beta} \, \sqrt{\frac{\pi}{\frac{\beta}{2} + \frac{\lambda}{2D}}} \right\} \right] \quad , \tag{5.2}$$

where we have assumed the linearized potential $V(x) = E_0 - \frac{1}{2}\omega_b^2 (x - x_0)^2$ at the barrier top in the expression for probability density function (4.25).

It is thus interesting to note that the quantum correction to classical population and flux at the semiclassical level ($\hbar^2$-order). These yield the expression for rate of escape (3.2) as

$$k = e^{-E_0/k_B T} \, \frac{\omega_0}{2\pi} \, \frac{\sqrt{\gamma^2 + \omega_b^2} - \gamma}{\omega_b} \, \left[1 + \hbar^2 \, \frac{A}{8 \, (k_B T)^{3/2}} \, \frac{1}{\sqrt{\gamma^2 + \omega_b^2} + \gamma} \right] \quad , \tag{5.3}$$

where we have put $\beta = 1/k_B T$, $\lambda = -\gamma + \sqrt{\gamma^2 + \omega_b^2}$ and A is the nonlinear parameter of the cubic potential (3.1).

The above expression can be rewritten as

$$k = k_{cl} \; + \; k_{semi} \quad , \tag{5.4}$$

where k_{cl} and k_{semi} correspond to classical and semiclassical Kramers' rate, respectively, with

$$k_{cl} = \frac{\omega_0}{2\pi} \, \frac{\sqrt{\gamma^2 + \omega_b^2} - \gamma}{\omega_b} \, e^{-E_0/k_B T} \quad , \tag{5.5a}$$

$$k_{semi} = \frac{\omega_0}{2\pi \omega_b} \, \left(\frac{A \hbar^2}{8 \, (k_B T)^{3/2}} \right) \, \left(\frac{\sqrt{\gamma^2 + \omega_b^2} - \gamma}{\sqrt{\gamma^2 + \omega_b^2} + \gamma} \right) \, e^{-E_0/k_B T} \quad . \tag{5.5b}$$

The result (5.3) describes the spatial diffusion controlled rate of escape at moderate to strong friction γ at the semiclassical level where the leading order quantum correction makes its presence felt. We also emphasize that since we are using high temperature ($k_BT > \hbar\omega$) semiclassical surrounding due to Caldeira and Leggett, the result cannot be extrapolated to zero temperature/low temperature limit, when non-Markovian effects also begin to influence the dynamics. The temperature dependence of $\hbar^2$-containing term in (5.3) signifies that as k_BT becomes large the quantum contribution significantly diminishes - a typical semiclassical feature in the dynamics, as expected. For $\gamma = 0$ the expression (5.3) yields the result of "simplest" transition state theory k_{TST} which includes the quantum correction at the semiclassical as well

$$k_{TST} = \frac{\omega_0}{2\pi} \left\{ 1 + \frac{\hbar^2 A}{8\,\omega_b\,(k_BT)^{3/2}} \right\} e^{-E_0/k_BT} \quad . \tag{5.6}$$

For the strong friction case, Eq.(5.3) can be simplified further to give the rate of escape in the overdamped regime ($\gamma \gg \omega_b$),

$$k_{overdamped} = \frac{\omega_0\omega_b}{2\pi} \left\{ \frac{1}{\gamma} + \frac{\hbar^2 A}{32\,\gamma^2\,(k_BT)^{3/2}} \right\} e^{-E_0/k_BT} \quad , \tag{5.7}$$

which approaches to zero as $\gamma \to \infty$. $\hbar^2$ term in the above expression reveals a stronger friction ($1/\gamma^2$) dependence, which implies that quantum correction term is more susceptible to damping. The classical limit of (5.7) is the Smoluchowski limit. Therefore the result (5.7) may be regarded as the semiclassical Smoluchowski-Kramers limit.

VI. CONCLUSIONS

The main purpose of this paper is to explore whether a differential equation (for probability distribution function) based approach is possible for calculation of quantum Kramers' rate. We show that Wigner-Leggett-Caldeira [WLC] equation which describes the quantum Brownian motion in a force field, in a high temperature Ohmic environment is suitable for this purpose. Based on an expansion in powers of $\hbar$ we solve this equation for Wigner probability density function of c-number variables under appropriate boundary conditions. We

make use of Wigner's quantum correction to Boltzmann factor to describe the thermalization of the particles deep inside the well. The effective dynamics is spatial-diffusion limited and the drift term (γ) is Markovian. The validity of the theory is ensured at high temperature and for the intermediate to strong damping regime, where the quantum corrections upto the order $\hbar^2$ significantly modifies the classical Kramers' results.

We now summarize the main conclusions of the study:

(i) We have identified WLC equation as a semiclassical Kramers' equation and calculated explicitly the barrier crossing dynamics. The method is closer to the classical one and is different from the existing path integral approaches for calculation of quantum Kramers' rate. While the existing procedure to calculate the total rate is to add k_{quant} to the classical Kramers' rate k_{cl}, the present method yields the total semiclassical rate. In the limit $\hbar/k_BT \to 0$ the classical rate is recovered.

(ii) The quantum correction to classical Kramers' rate includes $1/\gamma^2$ dependence in the overdamped limit ($\gamma \to \infty$).

(iii) The semiclassical theory can be reduced to 'simplest' quantum transition state description for $\gamma = 0$ situation. The rate becomes susceptible to the ratio of nonlinear coefficient to linear barrier frequency.

(iv) The role of nonlinearity gets entangled with quantum correction in this description. This is obvious from the appearance of the higher derivatives of the potential in the Wigner equation. The quantum noise term appears as a source term in classical equation.

(v) Kramers' celebrated ansatz in classical theory (the factorization of an equilibrium factor from a dynamical factor) is generalized in the present semiclassical context.

(vi) Compared to other existing methods the quantum-classical correspondence in the problem of barrier crossing dynamics is relatively more transparent in the present approach.

In view of the considerable development of the theory in the weak coupling limit, particularly in the quantum optical context, we believe that the Wigner function approach like the present one can be suitably extended to analyze the energy diffusion rate in the semiclassical domain in the Markovian limit. Since at low temperatures, the non-Markovian effects begin

to be appreciable, one feels the need for appropriate non-Markovian quantum Brownian equations. In absence of these descriptions any differential equation based approach is to remain far from promising.

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