Chemical Physics 431–432 (2014) 26–38

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Taming the escape dynamics of nonadiabatic time-periodically driven quantum dissipative system within the frame of Wigner formalism

Anindita Shit [a], Sudip Chattopadhyay [a,*], Jyotipratim Ray Chaudhuri [b,*]

[a] Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711103, India
[b] Department of Physics, Katwa College, Katwa, Burdwan 713130, India

ARTICLE INFO

Article history:
Received 11 September 2013
In final form 15 January 2014
Available online 23 January 2014

Keywords:
Time-periodic drive
Quantum dissipative system
Langevin and Fokker–Planck equations
Nonadiabatic escape rate
Crossover temperature

ABSTRACT

Escape under the action of the external modulation constitutes a nontrivial generalization of an conventional Kramers rate because the system is away from thermal equilibrium. A derivation of this result from the point of view of Langevin dynamics in the frame of Floquet theorem in conjunction with the Kapitza–Landau time window (that leads to an attractive description of the time-dependent quantum dynamics in terms of time-independent one) has been provided. The quantum escape rate in the intermediate-to-high and very-high damping regime so obtained analytically using the phase space formalism associated with the Wigner distribution and path-integral formalism bears a quantum correction that depends strongly on the barrier height. It is shown that an increase of (amplitude/frequency) ratio causes the system to decay faster, in general. The crossover temperature between tunneling and thermal activation increases in the presence of field so that quantum effects in the escape are relevant at higher temperatures.

1. Introduction

Activated escape over a potential barrier plays a fundamentally important role in many areas of physics, chemistry, diffusion in solids and on solid surfaces [1]. Apart from the well established applications, new and exciting applications of activated escape phenomena to biology and to nano-science have kept the subject at the forefront of current research, both theoretical and experimental [2–4]. Much effort has already been given to explore the unknown features associated with a plethora of phenomena shaping a host of biological processes [5]. The ion pumps, motor proteins and the likes are no longer contemplated as wind-up toys, they are rather true molecules with very specific functions that are dictated by switching on from one conformational motif to the other. As a consequence, these molecular processes strictly abide by the rules of chemical kinetics for surmounting the activation barrier that separates the two conformational states. This barrier crossing dynamics embodies a panorama of associated issues related to nonlinear dynamics and (internal and/or external) equilibrium as well as nonequilibrium perturbations.

Activation in the presence of time-varying fields has also become a subject of great interest due to the discovery of many counterintuitive noise-assisted effects [6,7]. Apart from its fundamental significance, motivation to study this problem arises from recent work on the dynamical strength of molecular bonds [8]. The underlying mechanism due to the external force is readily manipulated for adiabatically slow (low-frequency) periodic driving, where the system remains in quasi-stationary situation under the instantaneous value of the driving force. From a theoretical point of view, the probability distribution of particles always follows the Boltzmann form, and the second law of thermodynamics sets strict restrictions on the behavior of the system. For such a situation, the escape rate can at any time be approximated by the escape rate in the frozen system [6,9]. A completely different picture has emerged for the dynamics of a particle that is driven by a rapidly oscillating potential (ROP), where driving becomes nonadiabatic in nature due to the extremely complicated interplay between global properties of the metastable potential and the external driving. It is known that an additional external driving force applied to the Brownian particle can break the energy balance mechanism and make the composite system thermodynamically open. The direct consequence of this is the loss of the fluctuation–dissipation relation. The situation is much more demanding, as well as complicated and, despite its paramount importance, it has been studied much less extensively than the first one. On the other hand, the possible behavior of the modulated system is much more multifaceted, and decisive, often counterintuitive effects can occur [10–12]. For high-frequency (nonadiabatic) driving, the quantity of primary interest is the escape rate. A complete theoretical development for the nonadiabatic escape is still nontrivial and challenging, as one

* Corresponding authors.
E-mail addresses: sudip_chattopadhyay@rediffmail.com (S. Chattopadhyay), jprc_8@yahoo.com (J. Ray Chaudhuri).

http://dx.doi.org/10.1016/j.chemphys.2014.01.008
0301-0104/

may no longer assume that the system is in equilibrium and therefore worth pursuing [12–19].

Although the classical theory of escape of a Brownian particle from a metastable well is well developed and discussed [20–23], much less is known for the corresponding quantum mechanical model [24–27]. Unfortunately, at present, any well founded approach for barrier crossing process is not available in this regime. This is due to the fact that in the quantum regime, the interplay of quantum fluctuations in the bath and system dynamics yields long-range retardation effects in time, as a result of which the construction of general tractable equations of motion becomes very difficult [27–29].

The dynamics of a quantum Brownian particle in the very high damping (VHD) limit, where the underlying kinetic equation is the Smoluchowski equation, have been extensively investigated at various levels of description by a large number of workers [29–36]. The regime of the Smoluchowski limit corresponds to a separation of time scales between equilibration of momentum, which is fast, and equilibration of position, which is slow. In the limit of high friction (Smoluchowski limit), the velocity part of the phase space distribution of a Brownian particle quickly relaxes to equilibrium. The master equation for the time evolution of the Wigner distribution function in phase space provides a useful tool for the calculation of quantum corrections to classical models of dissipation such as Brownian motion (see, for example, [29,37–40]). As shown recently by Coffey et al. [29,32,33], the Wigner formalism can be used to derive a semiclassical form of the Smoluchowski equation. They proposed a method for the determination of the effective diffusion coefficient of a quantum Brownian particle based on the thermal Wigner distribution for the uncoupled system. Another very useful tool to describe nonequilibrium time-dependent dissipative phenomena is the path integral approach. The work by Ankerhold et al. [31] has shown how to take advantage of the path integral representation of quantum mechanics for a rigorous derivation of the quantum Smoluchowski equation (QSE). This equation has already been used in many applications of the quantum Brownian motion in a periodic potential [41–44]. It is enlightening to point out at this juncture that Ray Chaudhuri and coworkers [45] have demonstrated that their QSE is equivalent to those of Ankerhold et al. [31], Coffey et al. [29,32,33] and Dillenschneider et al. [36] for the harmonic oscillator case when terms up to $\hbar^2$ are being preserved. Despite the various methodological developments and numerous attempts in the past few decades for the quantum Smoluchowski equation of undriven systems, investigation for driven quantum systems still remains a challenge.

In our present work, we continue our study [17,18] in the presence of time-periodic rapidly oscillating single pulse. In our development, we have assumed that the driving frequency is very large, much larger than all other relevant system frequencies associated with the system dynamics and one can thus exploit Kapitza–Landau [46] time window that is based on a separation of the particle's motion into a 'slow' and a 'fast' changing part. Thereby, we obtain an effective time-independent dynamics of the system alone. For large frequency, the amplitude of the fast motion can be assumed to be small, since due to its inertia, the particle does not have the time to react to the force which is induced by the oscillating potential before this force changes sign. In Ref. [18], we have investigated the escape rate in the VHD region for a quantum particle moving in a time-periodic rapidly oscillating potential in the frame of path-integral approach. This brings to fore a new broad perspective for the study of activated processes in nonequilibrium open systems. Adopting our present method of effective quantum Brownian dynamics in presence of a ROP, we present in this paper, a careful study on the nonequilibrium activated barrier crossing process by exploiting Wigner phase space formalism. The aim of this paper is twofold: we first study the effect of a time-periodic ROP on the escape rate obtained via path-integral approach and Wigner's phase-space formulation [29,32,33] in the intermediate to high damping (IHD) and Smoluchowski limit. Second, the escape results so obtained using Wigner formalism will then be compared with those calculated from the QSE recently published by Shit et al. [18] from the path-integral representation of dissipative quantum mechanics due to Ankerhold and coworkers [31]. This comparison nicely portrays the effectiveness and flexibility of the quantum Smoluchowski equation emerged from the path integral and Wigner formulations of quantum dissipative systems.

2. General formulation for a rapidly varying time-periodic force in the frame of system–reservoir coupling environment

In this section, we shall investigate the dynamical behavior of a modulated quantum system in contact with a heat bath. In this case, the system has to be considered as an open system. The coupling with a heat bath causes damping of the quantum system and no longer is the dynamics predicted by the Schrödinger equation alone. As we have already stated, we focus on the result that on time scales larger than the period of perturbation, the dynamics is equivalent to one in which the periodic perturbation is replaced by a time independent effective potential. This important result is derived by Jung in Ref. [47] through a Fokker–Planck equation approach. Here, we briefly provide an alternative derivation of this result through the Langevin dynamics approach with special reference to the applications we will be dealing with in this paper. As the system is far from thermal equilibrium and cannot be characterized by Boltzmann distribution, the transition rate needs to be calculated from system dynamics. In order to be away from any restriction of amplitude or frequency of the driving force, and of the number of states in the potential, we treat the problem in the framework of the Floquet formalism [48,49].

For the sake of simplicity only, we restrict ourselves to the one-dimensional case. A generalization of the formalism to higher-dimensional cases is straightforward. We employ here the following system-reservoir Hamiltonian of Zwanzig form [9]:

$$\hat{H} = \hat{H}_S(\hat{x},\hat{p}) + \hat{H}_B(\{\hat{q}_j\},\{\hat{p}_j\}) + \hat{H}_{SB}(\hat{x},\{\hat{q}_j\}) = \frac{\hat{p}^2}{2m} + \sum_{j=1}^{N}\left\{\frac{\hat{p}_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2\left(\hat{q}_j - \frac{c_j\hat{x}}{m_j\omega_j^2}\right)^2\right\} + \hat{V}_0(\hat{x}) + \hat{V}_1(\hat{x},\omega t) \quad (1)$$

where the last two terms represent respectively the system and oscillating potentials with a vanishing time average (consequently, any interesting effect is due to the rapidly oscillating potential). $\hat{V}_1$ is a periodic function of ωt, which enables the use of the Floquet formalism and can be identified as $V_1(x,\omega(t+\tau)) = V_1(x,\omega t)$ and $\frac{1}{T}\int_0^T dt V_1(x,\omega t) = 0$. As mentioned earlier, when the external force changes significantly slowly in time, the system essentially remains in equilibrium with the instantaneous potential. If that is not the case, the solution to the problem becomes a lot more difficult because no general methodology is available [48]. In one such work, Smelyanskiy et al. [14] considered the canonical problem of an overdamped Brownian particle which is also subjected to a periodic force and a white Gaussian noise. They estimated the time dependent escape rate for arbitrary values of the driving frequency but subject to the constraint that the amplitude of forcing is small compared to the barrier height. Lehmann et al. [15] also attempted to estimate the escape rate for arbitrary amplitude and frequency in the frame of path integral formulation. In the limit of vanishing noise strength, although their results are exact, the model breaks down at higher frequencies for a given noise strength. It is this regime that our work deals with. In fact, here, we intend to calculate the escape rate in the parameter regime where the amplitude of