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THERMAL ACTIVATIONPROCESS IN HYDROGEN BONDS

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ABSTRACT

We study the Markovian process on parameterized approximate nonlinear one-dimensional double Morse potentials, used to describe the collective proton dynamics in one dimensional network of hydrogen bonds. Using Kramer's method, the first and second moment of the proton's dynamic is evaluated respectively in the case of over damping, intermediate damping and very low damping limit. We found out that in the case of an over damping limit and intermediate damping, the dynamics of the proton decrease when the curvature parameter increases. In the case of very low damping limit, the motion of the proton in the well became independent on the curvature parameter.

Keywords: Brownian motion, Markovian process,Kramer's theory, Over damping limit, Intermediate damping limit, Very low damping limit, Double Morse potentials, Hydrogen bonds.

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Contribution/ Originality

This study is one of very few studies which have investigated on the interaction between the heat bath and the hydrogen bonds chain subject to parameterized nonlinear one-dimensional double Morse potentials more precisely the dependence of some physicals quantities with the curvature parameter.

1. INTRODUCTION

Understanding the dynamic behavior of the models of linear chains of interconnected atoms, subjected to a substrate of Φ^4 like-potential (Sine-Gordon, double-sine-Gordon, double quartic, and double Morse potential), becomes the subject of many studies in recent years [1-4]. Among these models, hydrogen bonds (HB) chain subject to double Morse potential are shown as the more attracted model. In fact, the existence of rapid pathway in ~~(HB)~~ due to proton translocation from proton donor (ion with which proton in HB bridge is more tightly linked) to proton acceptor (ion with which proton in HB bridge is less tightly linked)~~,~~ is very important in many biological reactions such as protection against mutation in genetic coding of DNA, stability of the DNA helix structure, the reduction of temperature extremes in large bodies of water, ATP synthase, photosynthesis, metabolism and enzymatic processes [5, 6]. Moreover with the mechanism of the proton transfers from one molecule to another [5-7] that allows the parallel arrangement of the cellulose polymer chain; HB has attracted many studies in the field of bioenergetics. Interested by the dynamic of the HB wave propagation, trough past studies [8-10] it has been generalized that the protonic conductivity of HB is associated with two complementary processes: (1)The propagation of an ionic positive (or negative) defect when an excess of proton is transferred inside the bridge interchanging the role of the covalent and the hydrogen bonds with the adjacent groups X; (2)The propagation of a banding (Bjerrum) defect, according to which the additional degree of freedom allows the group X-H to rotate in such a way that the inter-bond proton transfer is possible along the HB chain.

In Ref, Zolotaryuk, et al. [7] the considered model has been used to investigate the proton transport by taking into account the degrees of freedom of the heavy-ion subsystem, where essential ingredients of the models are the realistic anharmonic ion-proton interaction in the HB, the harmonic coupling between the protons in adjacent hydrogen bonds, and thus the harmonic coupling between the nearest-neighbor heavy ions (an isolated diatomic chain with the lowest acoustic band) or instead a harmonic on-site potential for the heavy ions, both providing a bistability of the HB proton. Considering then the insufficiency of the coupled motion of the H and X atoms to lower the barrier enough to provide a free soliton regime, the work of ref [5] was carried out.

In this paper, we consider the HB model as a chain of alternating masses m and M with $m \leq M$ (where m is the mass of proton H^+ and M an eventual ion mass X^-) connected by massless springs subjected to double Morse potential $V(u,\varphi)$, surround by the heat bath. This model proceeds to investigate the thermal fluctuation where the ion forming the intra-bond proton potential is assumed to be fixed. With these considerations, we analyze the dependence of the escape rate, the first and the second moment of the proton (H^+) as a function of the curvature parameter β from the case of over damping limit (ODL) to very low damping limit (VLDL) through the intermediated damping limit (IDL) regime.

The paper is organized as follows: the Markovian process of the ODL for ~~(*HB*)~~ in approximate double Morse potential is investigated in section II. In section III, the IDL and VLDL of Kramer's theory of HB in approximate double Morse potential are presented. The work ended in section IV by the conclusion.

2. MARKOVIAN PROCESS OF OVER DAMPING LIMIT OF HYDROGEN-BONDS IN APPROXIMATE DOUBLE MORSE POTENTIAL

Here, the system is constructed as a one dimensional chain model interacting with heat bath [11, 12] described by the following Hamiltonian.

$$H = H_S + H_b \tag{2.1}$$

where:

$$H_S = \sum_n \left(\frac{1}{2} m\dot{q}_n^2 + \frac{1}{2} M\dot{Q}_n^2 + \frac{1}{2} k_p \left(q_{n+1} - q_n\right)^2 + \frac{1}{2} k_{ion}\left(\varphi_n\right)^2 + \frac{1}{2} k_{sub} Q_n{}^2 + V\left(u_n, \varphi_n\right) \right) \tag{2.2}$$

Is the Hamiltonian of the HB in parameterizing double Morse potential. $q_n(t)$ represents the dimensionless displacement of the nth proton (H^+) in the hydrogen bridge from middle of nth and (n+1)th ion (X^-) when these ions are at the equilibrium position and $Q_n(t)$ being the displacement of the nth ion from its equilibrium position. k_p, k_{ion}, k_{sub} are interaction constants between nearest-neighbor protons, ions and the ions chain with substrate respectively. The dots denote the differentiation with respect to time. The lattice variables U_n are defined such that

$$u_n = q_n - \frac{1}{2}\left(Q_n + Q_{n+1}\right) \quad \text{and} \quad \varphi_n = Q_{n+1} - Q_n \qquad (2.3)$$

The intra-bond proton energy $V(u_n,\varphi_n)$ is chosen as a pair of Morse potentials placed tail-to-tail [5-8]:

$$V(u_n,\varphi_n) = \left\{ \frac{\left[\cosh\left(\beta\left(\frac{1}{2} - r_0\right)\right) - \cosh(\beta u_n)\exp\left(-\frac{1}{2}\beta\varphi_n\right)\right]}{\cosh\left(\beta\left(\frac{1}{2} - r_0\right)\right) - 1} \right\}^2 \qquad (2.4)$$

The parameter β is the measure of the curvature along the direction of the potential, taken at $\varphi_n = 0$. r_0 is the distance at equilibrium. In this model we consider the one dimensional motion of the proton (H^+) moving in an approximate double Morse potential (as showed in Fig.1) and coupled to a heat bath when the ions (X^-) are fixed [6, 7]. In these considerations, the Hamiltonian (2.1) can be rewritten in the simple form:

$$H_s = \frac{1}{2}m\dot{u}_n^2 + V(u_n) \qquad (2.5)$$

With the double Morse potential (4):

$$V(u) = \left[\frac{\cosh(\beta/4) - \cosh(\beta u)}{\cosh(\beta/4) - 1}\right]^2 \qquad (2.6)$$

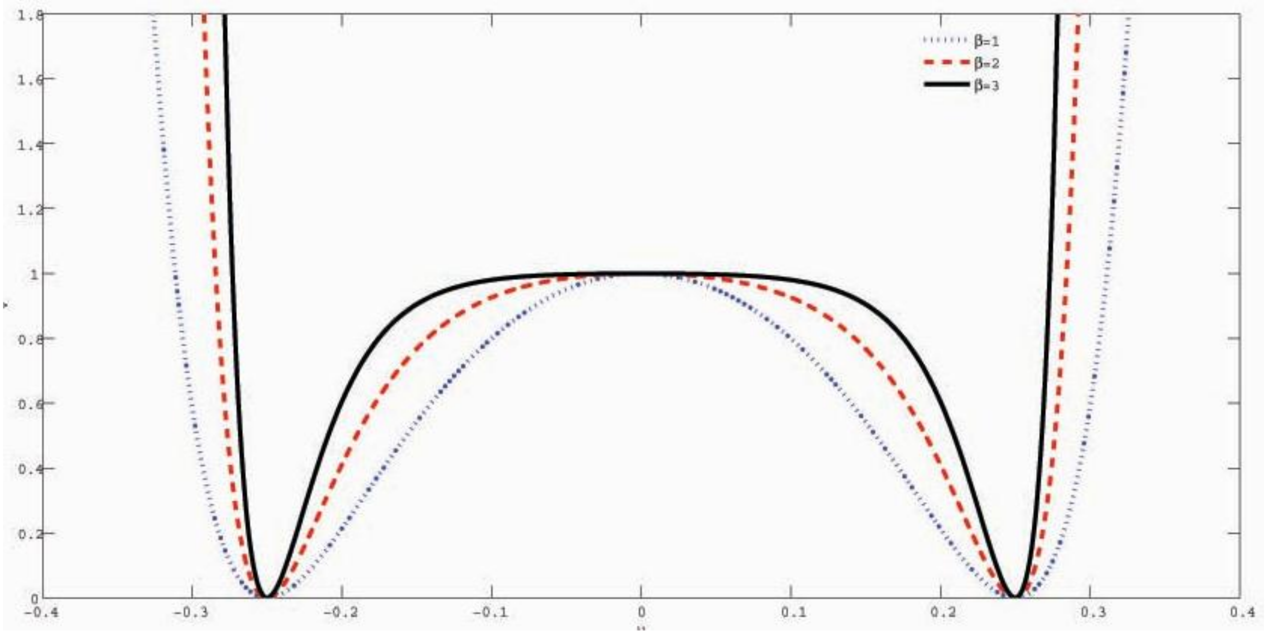

Fig-1. The shape of the intra-bond potential $V(u)$ with $r_0 = \frac{1}{4}$ *and* $\beta = 1,2$ *and*3

Equation (2.5) represents the Hamiltonian of the proton (H^+) in the potential well defined such that the mass m of proton is smaller as compared to the mass M of the ion X^- moving in a double Morse potential well (2.6) as illustrated in Fig.1.

$$H_b = \sum_\mu \left[\frac{1}{2m_\mu} p_\mu^2 + \frac{1}{2}k_\mu\left(x_\mu - u_\mu\right)\right] \qquad (2.7)$$

Equation (7) represents the heat-bath Hamiltonian with m_μ the mass of the particle in a bath, x_μ and p_μ the coordinate and momentum operators' force respectively. k_μ is the coefficient of interaction between the proton with each particle of the bath. To construct the dynamics of the system, the quantum Langevin equation is taken as the basis of the macroscopic description of the quantum particle linearly coupled to a heat bath [13-15]. Hence the Hamiltonian (2.1) is reduced to:

$$H=\frac{1}{2}m\dot{u}_n^2+V(u_n)+\sum_{\mu}\left[\frac{1}{2m_\mu}p_\mu^2+\frac{1}{2}k_\mu\left(x_\mu-u_\mu\right)\right] \qquad (2.8)$$

The corresponding quantum Langevin equation (QLE) associated with the dynamics of the system is given by [15-17]:

$$m\ddot{u}(t)+\int_{-\infty}^{t}\gamma(t-t')\dot{u}(t')dt'+\frac{\partial V(u)}{\partial u}=A(t) \qquad (2.9)$$

Where $A(t)$ is the random force that represented the collisions between the system and the bath, with the following statistical properties: $\prec A(t)\succ=0$ and $\prec A(t)A(t')\succ=K_BT\gamma(t-t')$.

The damping kernel $\gamma(t)$ describes the memory friction between the particle and the bath. $V(u)$ the substrate potential. Focalizing our study on the particular case where the particle in motion is subjected to instantaneous friction due to heat bath, the diffusion coefficient $\gamma(t-t')$ can be taken as:

$$\gamma(t)=\gamma\delta_+(t) \qquad (2.10)$$

With $\delta_+(t)$ the Dirac delta function. The approximation (2.9) brings the QLE (2.8) in the form

$$m\ddot{u}(t)+\gamma\dot{u}(t)+\frac{\partial V(u)}{\partial u}=A(t) \qquad (2.11)$$

In the over damping limit, the corresponding Langevin equation describing our system is:

$$\dot{u}(\tau)=-\frac{1}{\gamma}\frac{\partial V(u)}{\partial u}+\bar{A}(\tau) \qquad (2.12)$$

Here $\bar{A}(\tau)$ is the random force with the statistical properties $\prec\bar{A}(\tau)\succ=0$ describes and kernel

$$\prec\bar{A}(\tau)\bar{A}(s)\succ=k_BT\delta(\tau-s)$$

The breakaway of a particle over a potential barrier due to thermal fluctuation is a process characterized in classical limit by the escape rate. From the transition state theory (TST), the escape rate of a particle over a potential barrier is exponentially dependent on the temperature [17]. We discuss the breakaway of the ion particle H^+ through the potential barrier of the approximate double Morse-potential in HB due to thermal fluctuation. In the case of ODL, due to high friction, the proton will make a random motion inside the potential well. The breakaway of the proton will not able to deviate from the Boltzmann equilibrium the probability to find the particle at the top of the barrier; thus the particle would be able to do several oscillations at the top of the approximate double Morse potential barrier. In this section, we are concerned with the breakaway of the ion particle H+ through the potential barrier of the approximate double Morse-potential in HB due to thermal fluctuation in the case of (ODL).

To better illustrate our study, we mostly focus on the ODL and in the VLDL of the system with heat bath. The Fokker-Planck equation associated with the Langevin equation (2.10) is defined as Kelth and Chrlstlne [18]:

$$\frac{\partial W(u,\tau)}{\partial u}=\frac{\partial}{\partial u}\left[\frac{1}{\gamma}\frac{\partial V(u)}{\partial u}W(u,\tau)+k_B T\frac{\partial W(u,\tau)}{\partial u}\right] \qquad (2.13)$$

In order to investigate the thermal influence on the dynamics of the HB, we respectively evaluate the escape rate, the distribution probability, the first and second moment of the proton (H^+) inside the substrate potential given by (2.7). In fact, due to the dependence of Eq. (11) on the curvature parameter β and with the help of Kramer's method [18-21] the escape rate $r(\beta)$ of the proton in hydrogen-bonds is evaluated by:

$$r(\beta)=\frac{D\beta^2\sinh(\beta/4)}{\pi[\cosh(\beta/4)-1]^{3/2}K_B T}\exp\left(-\frac{1}{K_B T}\right) \qquad (2.14)$$

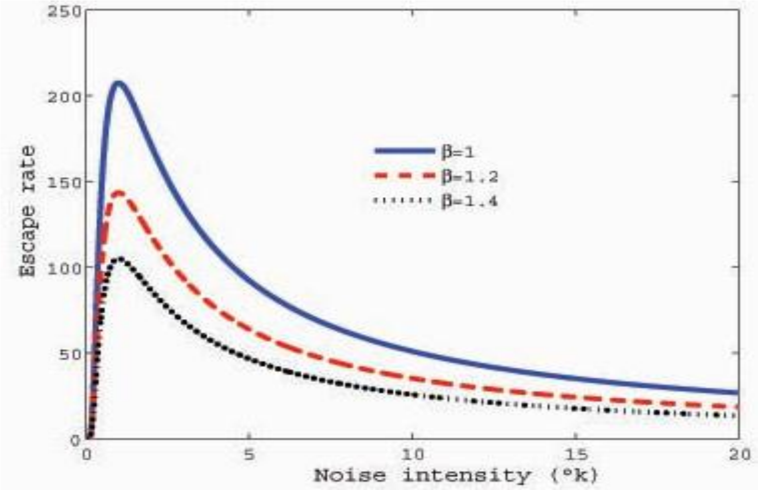

Fig-2. Escape rate versus temperature in the case of ODL

For this purpose, according to Kramer's theory the probability density function of the residence time distribution function [22]is given by

$$P(t)=r_k\exp(-r_k t) \qquad (2.15)$$

Where r_k is known as the Kramer's escape rate. Following Eq.(2.13), with the help of the Langevin equation and the statistical physics, the probability density function of the residence time distribution function is obtained as:

$$P_\beta(t)=\frac{D\beta^2\sinh(\beta/4)}{2\pi[\cosh(\beta/4)-1]^{3/2}\mu}\exp\left(-\frac{1}{2\mu}\right)\exp\left\{-\frac{2D\beta^2\sinh(\beta/4)}{\mu(\cosh(\beta/4)-1)^{3/2}\pi}\exp\left(-\frac{1}{2\mu}\right)t\right\} \qquad (2.16)$$

With $\mu=\frac{1}{2}K_B T$ the noise intensity. The first moment and the second moment associated with the residence time distribution are respectively defined by:

$$M1=\int_0^\infty tP(t)dt \tag{2.17}$$

and

$$M2=\int_0^\infty (t-M1)^2 P(t)dt \tag{2.18}$$

Hence by making use of equation (2.14), the first and second moment are given respectively [23, 24]by Eq.(2.19) and Eq.(2.20):

$$M_{1\beta}(\mu)=\frac{2\pi\mu(\cosh(\beta/4)-1)^{3/2}}{D\beta^2\sinh(\beta/4)}\exp\left(\frac{1}{2\mu}\right) \tag{2.19}$$

$$M_{2\beta}(\mu)=\frac{4\mu^2\pi^2(\cosh(\beta/4)-1)^3}{D^2\beta^4\sinh^2(\beta/4)}\exp\left(\frac{1}{\mu}\right) \tag{2.20}$$

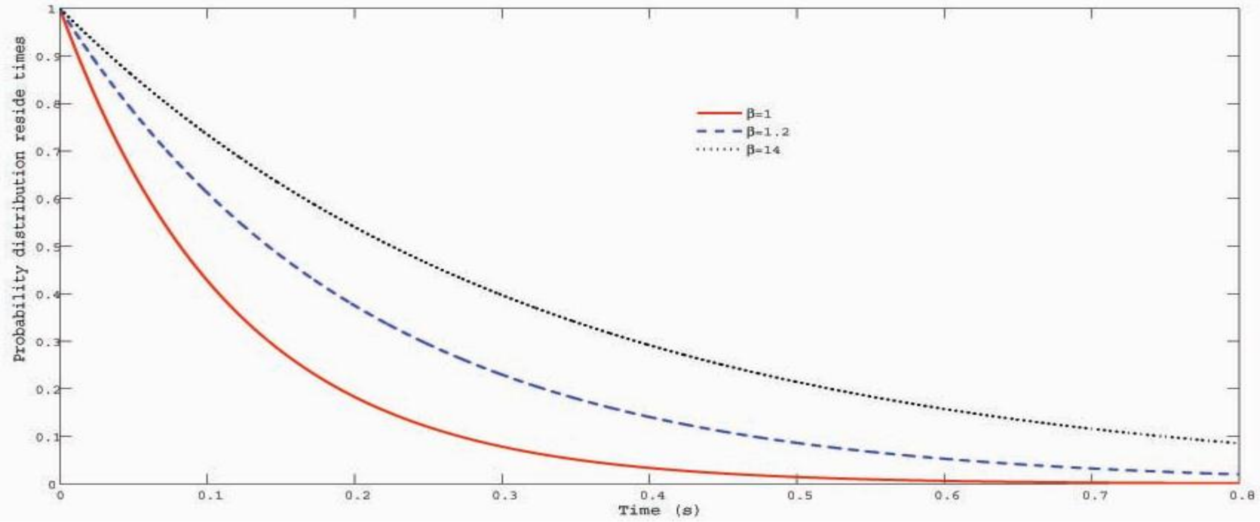

Fig-3. Density probability of residence time distribution function versus time in the case of ODL

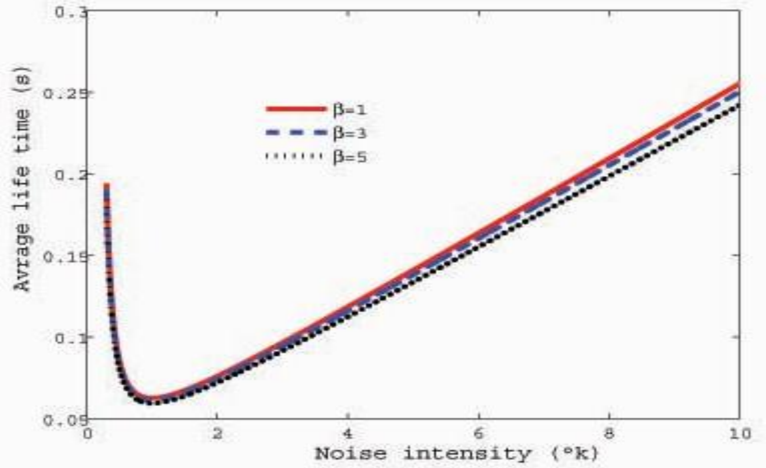

Fig-4. First moment versus noise intensity in the case of ODL

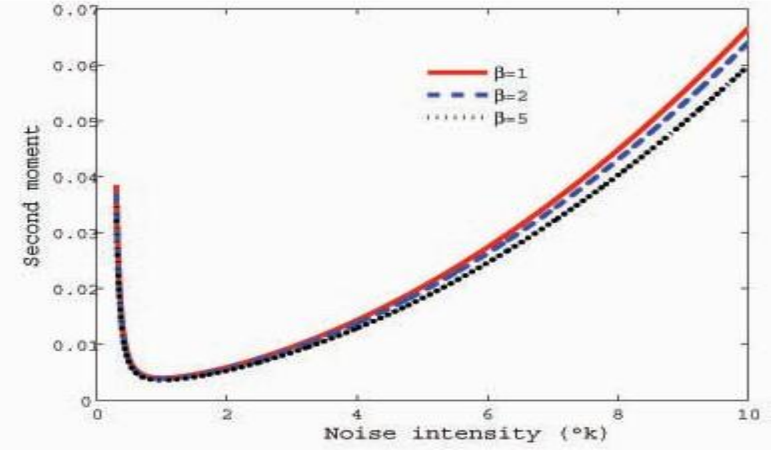

Fig-5. Second moment versus noise intensity in the case of ODL

3. MARKOVIAN PROCESS OF INTERMEDIATED AND VERY LOWDAMPING LIMIT

3.1. Markovian Process of IDL of Hydrogen-Bonds in Approximate Double Morse Potential

Based on the model where the heat-bath coupling causes a frictional force proportional to the velocity of the particle, the Langevin equation describing our system in the phase space is:

$$\begin{gathered}\dot{u}=v\\ \dot{u}=-\frac{\partial V(u)}{\partial u}-\gamma v+A(t)\end{gathered} \tag{3.1}$$

The Klein-Kramers' equation associated to Eq.(3.1) is:

$$\frac{\partial W(u,v,t)}{\partial t}=\left\{-v\frac{\partial}{\partial u}+\frac{\partial}{\partial v}\left[\gamma v+\frac{\partial V}{\partial u}\right]\right\}W(u,v,t)+k_B T\frac{\partial^2 W(u,v,t)}{\partial v^2} \tag{3.2}$$

From Eq(3.1) characterizing the model where the heat-bath coupling causes a frictional force proportional to the velocity of the particle, Kramer showed that the escape rate can be expressed in terms of the transition factor K [21, 22] as follows:

$$r=\frac{KW}{2\pi}\exp\left(\frac{\Delta V(u)}{2\mu}\right) \tag{3.3}$$

Where W is the oscillation frequency of the particle inside the well, and $\Delta V\ (u)$ the height of the potential barrier and the transition factor of approximated double Morse Potential is obtained as:

$$K=\left(\sqrt{1+\frac{1}{4Q^2}}-\frac{1}{2Q}\right) \tag{3.4}$$

With $Q(\beta)=\dfrac{\beta\sqrt{2}}{\gamma\sqrt{1-\cosh\left(\beta/4\right)}}$ the factor of quality. From Eqs (3.1),(3.2) and (3.4), the escape rate in IDL gives:

$$r_{IDL}(\mu)=\frac{\sinh\left(\beta/4\right)\left[\sqrt{\beta^2D^2+2\mu^2\left[1-\cosh\left(\beta/4\right)\right]}-D\mu\sqrt{1-\cosh\left(\beta/4\right)}\right]}{2D^2\left(\cosh\left(\beta/4\right)-1\right)}\exp\left(-\frac{1}{2\mu}\right) \tag{3.5}$$

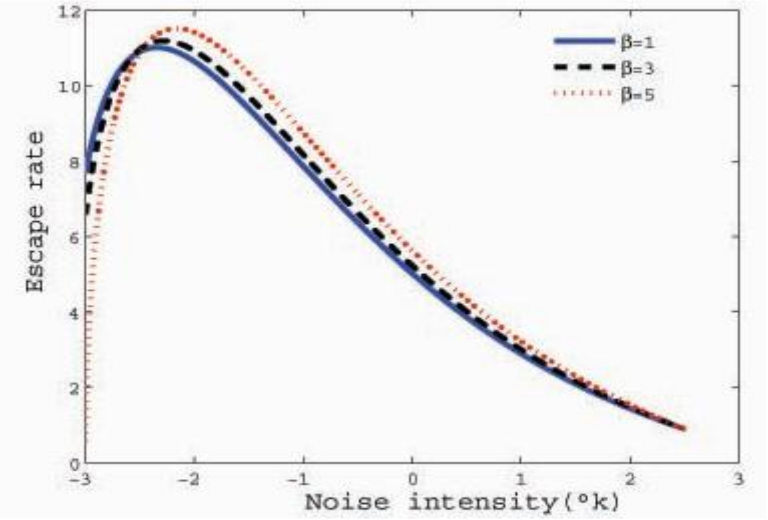

Fig-6. Kramer escape rate versus noise intensity in the case of IDL

Considering also Eqs. (2.14),(2.16), (2.17) and (3.5), the probability density function of the residence time distribution function, the first moment and the second moment of hydrogen-ion in the case of IDL are respectively given by:

$$p_{\beta}(t)=\frac{\sinh\left(\beta/4\right)\left[\sqrt{\beta^{2}D^{2}+2\mu^{2}\left[1-\cosh\left(\beta/4\right)\right]}-D\mu\sqrt{1-\cosh\left(\beta/4\right)}\right]}{2D^{2}\left(\cosh\left(\beta/4\right)-1\right)}e^{-\frac{1}{2\mu}}*$$

$$*\exp\left\{\frac{-\sinh\left(\beta/4\right)\left[\sqrt{\beta^{2}D^{2}+2\mu^{2}\left[1-\cosh\left(\beta/4\right)\right]}-D\mu\sqrt{1-\cosh\left(\beta/4\right)}\right]}{2D^{2}\left(\cosh\left(\beta/4\right)-1\right)}e^{-\frac{1}{2\mu}}t\right\} \qquad (3.6)$$

And

$$M_{1\beta}(\mu)=\frac{2D^{2}\left(\cosh\left(\beta/4\right)-1\right)}{\sinh\left(\beta/4\right)\left[\sqrt{\beta^{2}D^{2}+2\mu^{2}\left[1-\cosh\left(\beta/4\right)\right]}-D\mu\sqrt{1-\cosh\left(\beta/4\right)}\right]}\exp\left(\frac{1}{2\mu}\right) \qquad (3.7)$$

and

$$M_{2\beta}(\mu)=\frac{4D^{2}\left(\cosh\left(\beta/4\right)-1\right)^{2}}{\sinh^{2}\left(\beta/4\right)\left[\sqrt{\beta^{2}D^{2}+2\mu^{2}\left[1-\cosh\left(\beta/4\right)\right]}-D\mu\sqrt{1-\cosh\left(\beta/4\right)}\right]^{2}}\exp\left(\frac{1}{\mu}\right) \qquad (3.8)$$

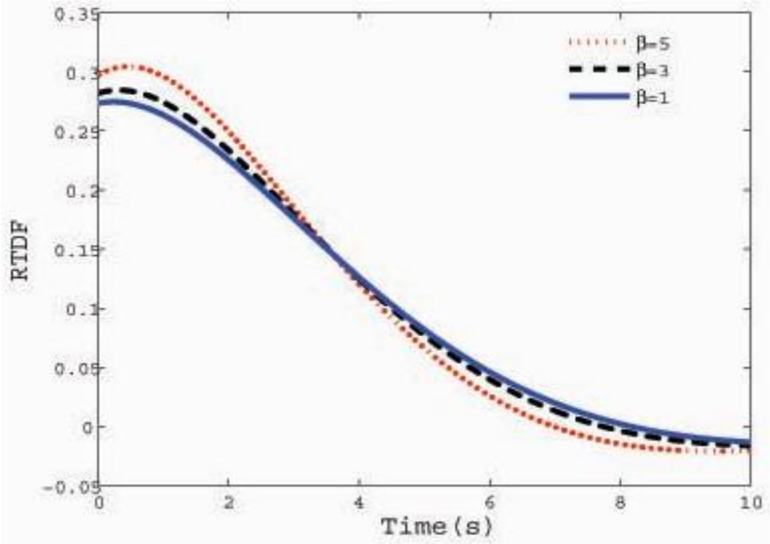

Figure-7. Probability density function of residence time distribution in the case of IDL

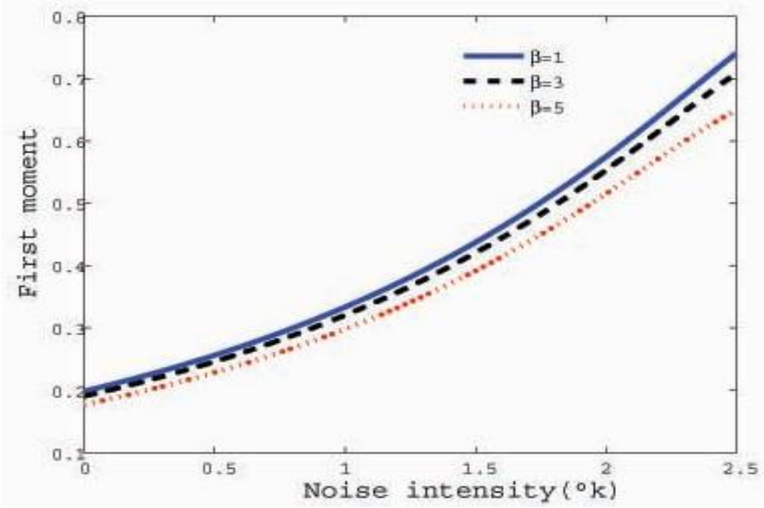

Figure-8. First moment versus noise intensity in the case IDL

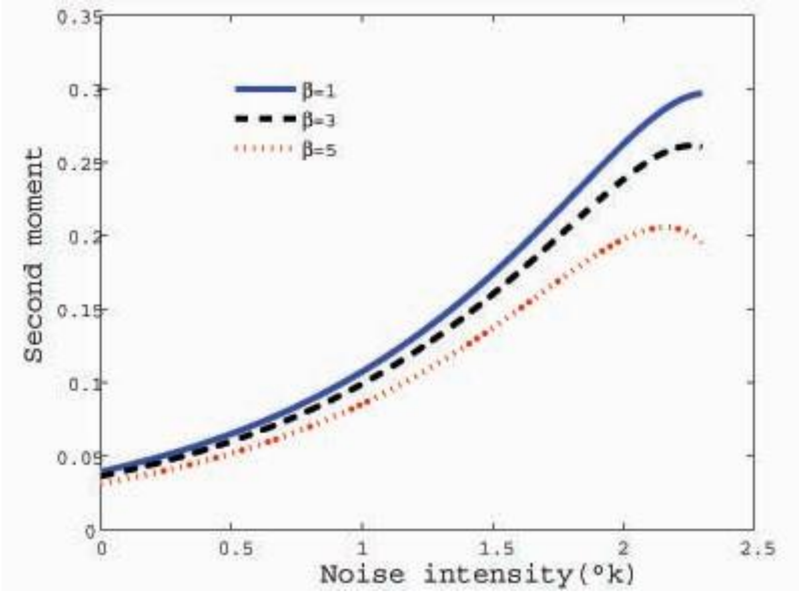

Fig-9. Second moment versus noise intensity in the case of IDL.

3.2. Markovian Process VLDL of Hydrogen-Bonds in Approximate Double Morse Potential

In this case, due to the very weak coupling to the heat bath, the fluctuating force is also weaken. That is, the hydrogen ion H^+ oscillates inside the approximated double Morse potential. In the presence of very low damping, the fluctuating forces cause variation of energy during the time of an oscillation. Therefore, the assumption that the Maxwell-Boltzmann is valid to a high degree of accuracy in the well is not valid. The restriction of the escape rate is due to the depletion of the probability to find the particle at the top of the potential barrier. Kramer discovers another way for calculating the escape rate when $\gamma I \prec\prec k_B T$ (with $I(E) = \oint P du$ the action integral around the curve of constant energy at the saddle point). The corresponding Klein-Kramer equation is:

$$\frac{\partial w(u,P,t)}{\partial t} = \left\{ -\frac{\partial V(u)}{\partial u}\frac{\partial W(u,P,t)}{\partial p} - P\frac{\partial W(u,p,t)}{\partial u} + \gamma \frac{\partial}{\partial P}\left[PW(u,P,t) + k_B T \frac{\partial W(u,P,t)}{\partial P} \right] \right\}$$

Hence the escape rate, the probability density function of the residence time distribution function, the first moment and the second moment in approximate double Morse potential are respectively evaluated from Eqs (3.9), (2.14), (2.16) and (2.17):

$$r = \frac{\gamma}{2\mu}\exp\left(-\frac{1}{2\mu}\right) \tag{3.10}$$

$$P_{VLDL}(t) = \frac{\gamma}{2\mu}\exp\left(-\frac{1}{2\mu}\right)\exp\left\{-\frac{\gamma}{2\mu}e^{-\frac{1}{2\mu}}\right\} \tag{3.11}$$

$$M_1(\mu) = \frac{2\mu}{\gamma}\exp\left(\frac{1}{2\mu}\right) \tag{3.12}$$

$$M_2(\mu) = \frac{4\mu^2}{\gamma^2}\exp\left(\frac{1}{\mu}\right) \tag{3.13}$$

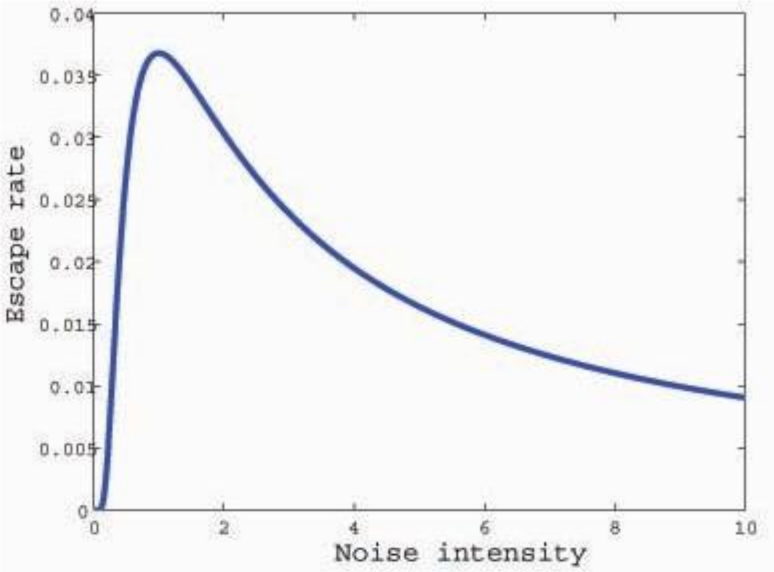

Figure-10. Kramer escape rate in the case of VLDL

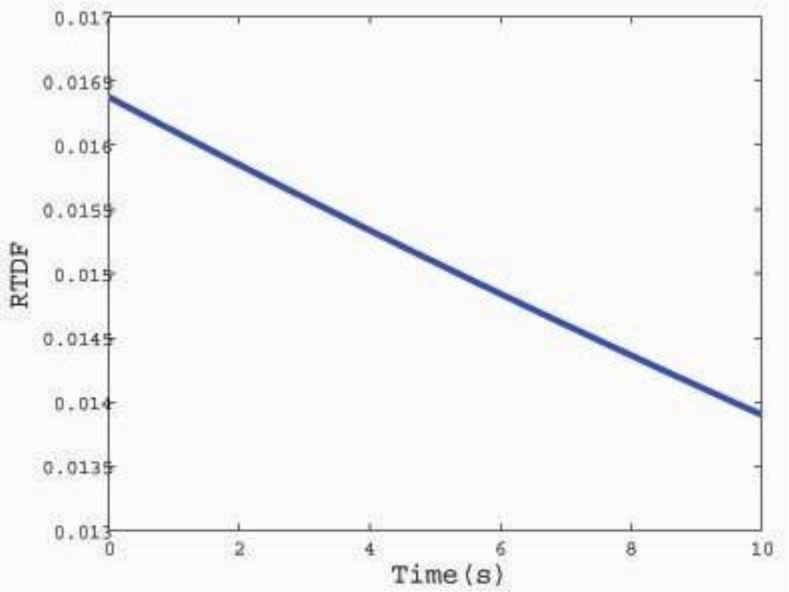

Fig-11. Probability density of residence time distribution in the case of VLDL

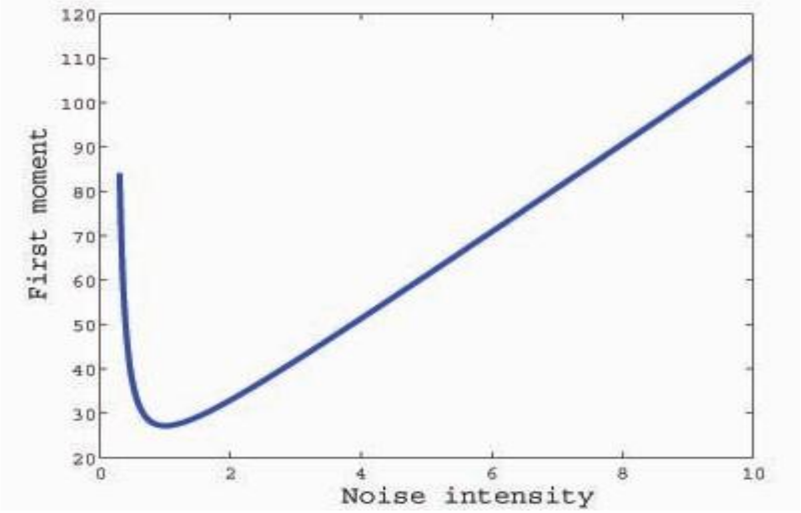

Fig-12. First moment versus noise intensity in the case of VLDL

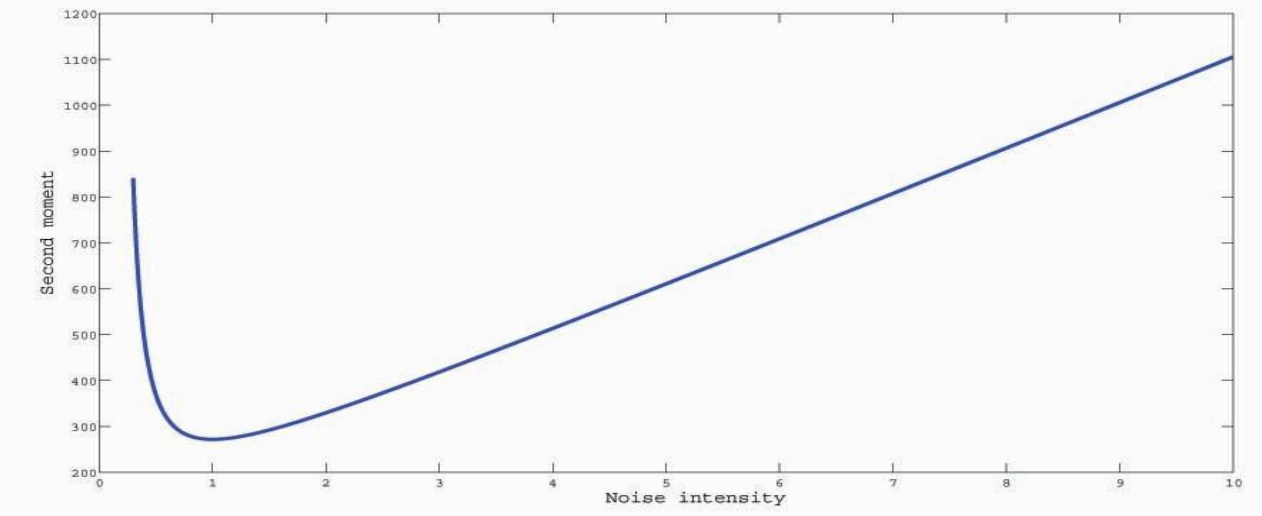

Fig-13. Second moment versus noise intensity in the case of VLDL

4. CONCLUSION

We have modeled the thermal activated process of hydrogen bonds by considering the one dimensional network of hydrogen bonds in interaction (from over to very low through intermediate damping limit) with a heat bath when the ions (X^-) are fixed. By means of Kramers' method, we have analytically determined the escape rate, the time distribution function, the first and the second moment of the proton in all damping regime. In the case of over damping limit and intermediate damping limit, the above physical quantities strongly depend on the curvature parameter β and they decrease when the curvature parameter βincreases. Thus more the barrier is flat and the wells more narrow, it became easy for the proton (H^+) to break away from one well to another. In the case of very low damping limit the motion of the proton inside the well is independent β.

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REFERENCES

[1] M. Nznojil, "The perturbated sine-gordon equation," *ACTA Physica Polonica*, vol. B 10, pp. 951-958, 1979.

[2] A. M. Dikande, "Kink dislocations in layered lattices with periodic interlayer substrate interactions," *Phys. Stat. Sol.*, vol. 208, pp. 5-14, 1998.

[3] S. Rainer, K. S. Yuri, S. Angel, and B. R. Alan, "Sine-gordon kink-antikink generation on spatially periodic potentials generation," *Phys. Rev. A*, vol. 45, pp. R5369-R5372, 1992.

[4] V. Anna and K. G. Panayotis, "Dynamics of phase transitions in a piecewise linear diatomic chain," *J. Nonlinear Sci.*, vol. 22, pp. 107-134, 2012.

[5] N. A. S. Tchakoutio and T. C. Kofane, "Soliton patterns and breakup thresholds in hydrogen-bonded chains," *Eur. Phys. J. B*, vol. 57, pp. 411–422, 2007.

[6] V. M. Karpan, Y. Zolotaryuk, P. L. Christiansen, and A. V. Zolotaryuk, "Discrete kink dynamics in hydrogen-bonded chains: The two-component model," *Phys. Rev.*, vol. E 70, pp. 1-11, 2004.

[7] A. V. Zolotaryuk, M. Peyrard, and K. H. Spatschek, "Collective proton transport with weak proton-proton coupling," *Phys. Rev. E*, vol. 62, pp. 1-5, 2000.

[8] R. Grauer, K. H. Spatschek, and A. V. Zolotaryuk, "Chaotic proton dynamics in the hydrogen bond," *Phys. Rev. E*, vol. 47, pp. 236-247, 1993.

[9] B. Malin, W. Jakob, H. E. Michael, and B. W. John, "Simulation studies of the insolubility of cellulose," *Carbohydrate Research*, vol. 345, pp. 2060–2066, 2010.

[10] W. A. Colin, "Chance and design—proton transfer in water, channels and bioenergetic proteins," *Biochimica et Biophysica Acta*, vol. 1757, pp. 886–912, 2006.

[11] G. W. Ford, J. T. Lewis, and R. F. O'connell, "Quantum langevin equation," *Phys. Rev. A*, vol. 37, pp. 4419-4428, 1988.

[12] P. Elie, "Variational transition state of reaction rate in dissipative system," *Phys. Rev. Lett.*, vol. 67, pp. 1399-1402, 1990.

[13] H. H. Risken, *The Fokker-Planck equation. Springer series in synergetics* vol. 18. Berlin: Springer-Verlag, 1934.

[14] M. Tchoffoet, "Kinematical brownian motion and time dependent entropy," *Far East Journal of Applied Mathematics*, vol. 68, pp. 21-28, 2012.

[15] P. Elie, G. Hermann, and H. Peter, "Theory of activated rate process for arbitrary frequency dependent friction: Solution of the turnover problem," *J. Chem. Phys.*, vol. 84, pp. 4073-4087, 1986.

[16] J. C. Latorre, G. A. Pavliotis, and P. R. Kramer, "Corrections to einstein's relation for Brownian motion in a tilted periodic potential," *J. Stat. Phys.*, pp. 1-28. Doi: 10.1007/s10955-013-0692-1, 2012.

[17] H. Peter and H. Waldemar, "Tunneling in reaction theory: The effect of memory friction," *Physica Scripta*, vol. 37, pp. 559-563, 1988.

[18] L. J. Kelth and K. M. Chrlstlne, "The development of transition-state theory," *J. Phys. Chem.*, vol. 87, pp. 2657-2664, 1983.

[19] G. Hermann, "Escape from a metastable well: The Kramers turnover problem," *Phys. Rev. Lett.*, vol. 61, pp. 1683-1686, 1988.

[20] M. J. R. Antonio and H. Peter, "Escape from a fluctuating double well," *Phys. Rev. E*, vol. 51, pp. 3849-3861, 1995.

[21] C. Srabanti and C. J. Binny, "Approximate first passage time distribution for barrier crossing in a double well under fractional Gaussian noise," *J. Chem. Phys.*, vol. 125, pp. 1-8, 2006.

[22] L. Benjamin, "Correlations in the sequence of residence times," *Phys. Rev. Lett.*, vol. 98, pp. 1-4, 2007.

[23] J. L. Vega, R. Guantes, and S. Miret-Arte´s, "Mean first passage time and the Kramers turnover theory in activated atom–surface diffusion," *Phys. Chem. Chem. Phys.*, vol. 4, pp. 4985–4991, 2002.

[24] C. T. William, K. P. Yuri, and T. V. Sergey, "Thermally activated escape rate for the Brownian motion of a fixed axis rotator in a double well potential for all values of the dissipation," *J. Chem. Phys.*, vol. 120, pp. 9199-9211, 2004.