Crossover from thermal hopping to quantum tunneling in $Mn_{12}Ac$

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The crossover from thermal hopping to quantum tunneling is studied. We show that the decay rate Γ with dissipation can accurately be determined near the crossover temperature. Besides considering the Wentzel-Kramers-Brillouin (WKB) exponent, we also calculate contribution of the fluctuation modes around the saddle point and give an extended account of a previous study of crossover region. We deal with two dangerous fluctuation modes whose contribution cannot be calculated by the steepest descent method and show that higher-order couplings between the two dangerous modes need to be taken into consideration. At last the crossover from thermal hopping to quantum tunneling in the molecular magnet $Mn_{12}Ac$ is studied. [S0163-1829(99)03409-8]

I. INTRODUCTION

The decay of metastable states in macroscopic systems is a fundamental problem in many areas of physics, such as macroscopic quantum tunneling in Josephson systems,[1,2] violation of baryon-lepton in Weinberg-Salam model, nucleation in first order phase transition theory,[3,4] and, more recently magnetic quantum resonant tunneling.[5] The crossover from thermal hopping to quantum tunneling has been studied intensively. Using the functional integral approach, Affleck first demonstrated the transition can be found between classical regime and quantum regime.[6] Larkin and Ovchimikov also suggested it and gave a formula determining the boundary of first- and second-order transition.[7,8] Grabert and Weiss discussed the phase transition in the presence of dissipative effects of the environment in some detail.[9–11]

At high temperature, the decay of the metastable state is determined by process of thermal activation, which is governed by the Arrhenius law, $(\omega_0/2\pi)\exp(-\Delta U/T)$, where $\omega_0=\sqrt{-U''(x_0)/M}$ is the well frequency and ΔU is the barrier height. While at $T=0$ the particle can escape from the metastable state due to quantum tunneling, the rate of which goes as $\exp(-B)$ where B is the Wentzel-Kramers-Brillouin (WKB) exponent. Ignoring the prefactor and equating the exponents, one obtains the estimate

$$T_0^{(0)}=\frac{\Delta U}{B}, \tag{1.1}$$

where the superscript at T_0 means that the ground-state tunneling is considered. For $T>T_0^{(0)}$, one has practically $\Gamma \cong \Gamma_{therm}(T)$, whereas below the transition $\Gamma \cong \Gamma_{quan}$ is independent of temperature.

It turns out that for common metastable or double-well potentials, such as cubic or quartic parabola, below the crossover temperature T_0 the particles cross the barrier at the most favorable energy level $E(T)$ which goes down from the top of the barrier to the bottom of $U(x)$ with lowering temperature. The second-order transition from the classical thermal activation to thermally assisted tunneling (TAT) is smooth and the transition temperature is given by

$$T_0^{(2)}=\frac{\omega_b}{2\pi}, \tag{1.2}$$

where $\omega_b=\sqrt{-U''(x_b)/M}$ is the barrier frequency, and x_b corresponds to the top (the saddle point) of the barrier.

In Ref. 12, Chudnovsky stressed the analogy of this kind of transition phenomena with ordinary phase transitions and analyzed the general conditions for both types of quantum classical transitions. For the second-order transition the period of oscillation $\tau(E)$ in the inverted potential $-U(x)$ increases monotonically with energy E from the top of the barrier. If $\tau(E)$ is not monotonic, the first-order transition occurs. The escape rate can be conveniently represented in terms of the effective temperature defined by

$$\Gamma \sim \exp\left[-\frac{\Delta U}{T_0^{(1)}}\right]=\exp[-S_{\min}/\hbar]. \tag{1.3}$$

The actual dependence of $S_{\min}(T)$ goes along the minimum of these two actions (sphelaron and periodic instantons) and the first-order transition occurs at $T=T_0^{(1)}$. The first deriva-

tive of $S_{\min}(T)$ is discontinuous at $T_0^{(1)}$, providing that the crossover from the thermal to the quantum regime is the first-order transition.

The second-order transitions are common, whereas the first-order ones are exotic and have to be specially looked for. Nevertheless, a number of systems and processes that show first-order transitions are already known, e.g., a superconducting quantum interference device with two Josephson junctions,[13] false vacuum decay in field theories,[4,14–16] and depinning of a massive string from a linear defect.[17–22] All these systems have more degrees of freedom than just a particle, thus the search for a physical system equivalent to a particle in a potential $U(x)$ leading to the first-order transition of the escape rate seems quite actual. Qualitatively it is clear what $U(x)$ looks like: the potential should change slowly near the top and the bottom, but is rather steep in the middle. In this case, as for the rectangular barrier, tunneling just below the top of the barrier is *unfavorable*, the TAT mechanism is suppressed, and the thermal activation competes with the ground state tunneling directly, leading to the first-order transition.

Quantum tunneling of the magnetization (QTM) has become a focus of interest in physics and chemistry because it can provide a signature of quantum-mechanical behavior in a macroscopic system.[5] At low enough temperature, it has been demonstrated that the vector of the magnetization formed by a large number of spins in magnetic system can coherently tunnel between the degenerate minima of magnetic energy. Theoretical suggestions have led to a number of experiments which seem to support the idea of magnetic tunneling. Since the $Mn_{12}Ac$ complex magnetic molecule provides a more suitable model for the magnetic quantum tunneling, extensive works have been performed to demonstrate the QTM in large spin molecules.[25–27] On the other hand, the $Mn_{12}Ac$ molecule is one of the very few examples which could exhibit the first-order transition.

We derived a compact formula for decay rate which is valid for the entire range of parameters of interest in the problem of MQT. The quantum classical transitions of the escape rates in the dissipation systems are investigated by the periodic instanton method. Applying the periodic instanton method, we showed that the first-order transitions occur below the critical external magnetic field $h_x=\frac{1}{4}$ for $Mn_{12}Ac$ molecule which is in good agreement with earlier works.[28,29] The results of the application of a previous method is developed for dealing with the quasizero modes and calculating of decay rate in the crossover region which is beyond the steepest descent method.[9–11] In the crossover region of second-order transition $h_x>\frac{1}{4}$, we take fourth-order terms into account to include nonlinear couplings between the modes and obtain the universal law in this region. The point $h_x=\frac{1}{4}$ is the boundary of first order and second order. At this point the fourth-order couplings between modes disappear and sixth-order terms must be considered. For $h_x<\frac{1}{4}$ before the eigenvalues of the two quasizero modes reach zero, the first-order transition occurs and there is no universal law in common. While $T_0^{(1)}$ is not far from $T_0^{(2)}$ (such as $T_0^{(1)}=1.078T_0^{(2)}$ for $h_x=0.1$), the two dangerous modes also play important roles on the tunneling rate and need to be calculated carefully.

II. DECAY RATE IN THE CROSSOVER REGION OF SECOND-ORDER TRANSITION

The partition function can be written as a functional integral over periodic paths where the path probability is weighted according to the Euclidean action

$$S=\int_0^{\beta\hbar} d\tau\left[\frac{1}{2}M\dot{x}^2+U(x)\right]+\frac{1}{2}\int_0^{\beta\hbar} d\tau\int_0^{\beta\hbar} d\tau' k(\tau-\tau')x(\tau)x(\tau'), \quad (2.1)$$

where $k(\tau)=(1/M\beta\hbar)\Sigma_{n=-\infty}^{\infty}\xi(\nu_n)\exp(i\nu_n\tau)$, $\nu_n=2\pi n/\beta\hbar$, and $\xi(\nu_n)=\gamma(\nu_n)|\nu_n|$ is related to the frequency dependent damping coefficient $\gamma(\nu_n)$. $U(x)$ is a metastable potential with a local minimum at $x=0$ and a local maximum at $x=x_b$. We use ω_R to denote the solution of the following equation $\omega_R^2+\omega_R\gamma(\omega_R)=\omega_b^2$ where $\omega_b=\sqrt{-U''(x_b)/M}$ characterizes the width of the parabolic top of the well. In classical limit, $1/\hbar\to\infty$, the steepest descents method is available:

$$\delta S[x(\tau)]=0, \quad x(0)=x(\beta\hbar). \quad (2.2)$$

The fluctuation modes about the saddle point are expanded using Ψ_n, $x=x_c(\tau)+\Sigma_n Y_n\Psi_n$, where Y_n are fluctuation amplitudes and Ψ_n are modes of the spectrum:

$$-\ddot{\Psi}_n+U[x_c(\tau)]\Psi_n=\omega_n^2\Psi_n, \quad (2.3)$$

$$\Psi(\beta\hbar)=\Psi(0).$$

According to the metastable decay theory, quantum tunneling rate has the form $\Gamma=-(2/h)ImF$. Above the crossover temperature T_c, the decay process comes from the thermal activation $\Gamma=(2/\hbar)(\beta/\beta_c)ImF$ where $\beta_c=2\pi/\omega_R$.[6] In an ordinary case, the one-loop correction which results in a prefactor of the WKB leading-order exponential does not enhance the tunneling significantly and the transition rate is dominated by the WKB leading-order exponential. Near transition point the imaginary part of the free energy has a common form:

$$I_mF=-\frac{1}{2\beta}\left(\frac{\omega_0}{\omega_b}\right)\frac{\omega_1^{(0)2}}{\Lambda}f_c[\omega_0,\omega_b]\exp\left(\frac{-S_c}{\hbar}\right), \quad (2.4)$$

where S_c is just the WKB leading-order exponent, $\omega_n^{(0)2}=\omega_0^2+\nu_n^2+\nu_n\gamma(\nu_n)$, $\omega_n^{(b)2}=-\omega_b^2+\nu_n^2+\nu_n\gamma(\nu_n)$, $1/\Lambda$ comes from the two quasizero modes which need to be calculated carefully, and

$$f_c[\omega_0,\omega_b]=\prod_{n=2}^{\infty}\left[\frac{\omega_n^{(0)}}{\omega_n^{(b)}}\right]^2 \to\frac{\Gamma\left(2-\frac{\lambda_b^+}{\nu_1}\right)\Gamma\left(2-\frac{\lambda_b^-}{\nu_1}\right)}{\Gamma\left(2-\frac{\lambda_0^+}{\nu_1}\right)\Gamma\left(2-\frac{\lambda_0^-}{\nu_1}\right)} \quad \text{if } \gamma\equiv\text{const}, \quad (2.5)$$

where $\lambda_b^{\pm}=-\gamma/2\pm[\gamma^2/4+\omega_b^2]$, $\lambda_0^{\pm}=-\gamma/2\pm[\gamma^2/4-\omega_0^2]$ and $\omega_0=\sqrt{-U''(0)/M}$. Years ago Grabert and Weiss dis-

cussed the transition rate in the presence of dissipative effects of the environment in some detail.[9–11] They found an unstable mode besides the zero mode near transition point and calculated it carefully.[7–11] Near phase-transition point the fluctuation modes about the saddle points include two dangerous modes whose contribution can't be calculated by the steepest descent method and it is necessary to consider higher-order couplings between the two dangerous modes.[7–11]

A. Beyond steepest descent for $T>T_0^{(2)}$

Above $T_0^{(2)}$, the decay process is dominated by the saddle point called sphelaron $x=x_b$. Considering the fluctuation modes around it, we have the periodic paths near the saddle point[9–11]

$$x=x_b+Y_0+Y_{-1}\sqrt{2}\sin\frac{2\pi}{L}\tau+Y_1\sqrt{2}\cos\frac{2\pi}{L}\tau+\cdots \tag{2.6}$$

$$+Y_{-n}\sqrt{2}\sin\frac{2\pi n}{L}\tau+Y_n\sqrt{2}\cos\frac{2\pi n}{L}\tau. \tag{2.7}$$

There is a mode with negative eigenvalue $\omega_0^{(b)2}=-\omega_b^2=U''/M$ which is the key mode giving contribution to the imaginary part of the free energy. From the steepest descent method the result of the partition function of sphelaron solution is written into

$$\begin{aligned}Z&=\int_{x(0)=x(\beta\hbar)=0}D[x(\tau)]\exp\left\{\frac{-S[x(\tau)]}{\hbar}\right\}\\&=N\int\prod_n dY_n\exp\left\{\frac{-S[Y_n]}{\hbar}\right\}\\&=\frac{1}{2i}\frac{1}{\sqrt{\beta\hbar|\omega_b^2|}}\frac{N}{\sqrt{\beta\hbar\sum_{n\neq 0}\omega_n^{(b)2}}}e^{-S_c/\hbar},\end{aligned} \tag{2.8}$$

where $N=\sqrt{\omega_0^{(0)2}}\sqrt{\Sigma_{n\neq 0}\omega_n^{(0)2}}/2\sinh(\beta\omega_0/2)$.[29] The eigenvalues of the two lowest positive modes are $\lambda_1=\omega_1^{(b)2}=\omega_{-1}^{(b)2}=\nu_1^2-\omega_R^2$. Second-order transition occurs when the eigenvalue of the lowest modes is equal to zero $\lambda_1=0$ as temperature decreases, so it is defined that $T_c=\omega_R/2\pi$. Near the transition point, the eigenvalue of the lowest positive modes is

$$\lambda_1=-a\varepsilon, \tag{2.9}$$

where $\varepsilon=(1-T/T_c)$ and $a=\omega_b^2+\omega_R^2[1+\partial\gamma(\omega_R)/\partial\omega_R]$.

To regularize the divergent integral we have to add terms of fourth order in the amplitudes $Y_{\pm 1}$. After expanding the potential about the barrier top,

$$U(x)=\Delta U-\frac{M\omega_b^2x^2}{2}+\sum_i c_ix^i, \tag{2.10}$$

where $c_i=U^{[i]}(x=x_b)/i!$, we obtain the action

$$\begin{aligned}S[q]&=\int_0^{\beta\hbar}d\tau\left[\frac{1}{2}\left(\dot{x}_c(\tau)+\sum_n Y_n\dot{\Psi}_n\right)^2\right.\\&\quad\left.+V\left(x_c(\tau)+\sum_n Y_n\Psi_n\right)\right]\\&=\hbar\beta\Delta U+\frac{1}{2}\hbar\beta m\left[\sum_{n=-\infty,n\neq\pm 1}^{\infty}\omega_n^{(b)2}Y_n^2\right]+\Delta S,\end{aligned} \tag{2.11}$$

where

$$\Delta S=\beta\hbar\left[\frac{1}{2}m\omega_1^{(b)2}Y_1^2+\frac{1}{2}m\omega_{-1}^{(b)2}Y_{-1}^2+B_4(Y_1^2+Y_{-1}^2)^2\right]. \tag{2.12}$$

$B_4=\frac{3}{2}c_4+(9c_3^2/2M\omega_b^2)-(9c_3^2/4M\omega_2^{(b)2})$ and $\omega_2^{(b)2}=4\nu^2-\omega_R^2\simeq 3\omega_R^2$. After integrating the amplitudes Y_0 and Y_n, we deal with the quasizero modes to consider the fourth term: $B_4(Y_1^2+Y_{-1}^2)^2$. Introducing the polar coordination $\rho\cos\theta=Y_1$, $\rho\sin\theta=Y_{-1}$, we get

$$\begin{aligned}\frac{1}{\Lambda}&=\frac{\beta}{2\pi}\int dY_1\,dY_{-1}\exp-(\beta\Delta S)\\&=\frac{\kappa\sqrt{\pi}}{2\omega_R^2}\mathrm{erfc}(-\kappa\varepsilon)\exp(\kappa^2\varepsilon^2),\end{aligned} \tag{2.13}$$

where $\kappa=(M\omega_R^2/2)\sqrt{(\beta/B_4)}$. $B_4=\frac{3}{2}c_4+(9c_3^2/2M\omega_b^2)-(9c_3^2/4M\omega_2^{(b)2})=0$ has been defined as the boundary between the first-order transition and the second-order one in Ref. 7. For $B_4<0$ the integration in Eq. (2.12) is divergent and this kind of divergence will be discussed in first-order transition cases. It is obvious that the dissipation may change the boundary between the first-order transition and the second-order one. Then we have the transition rate from Eqs. (2.4) and Eq. (2.5):

$$\Gamma=\frac{\omega_0}{2\pi}\omega_1^{(0)2}\frac{\kappa\sqrt{\pi}}{2\omega_R^2}\mathrm{erfc}(-\kappa\varepsilon)\exp(\kappa^2\varepsilon^2)f_c[\omega_0,\omega_b]e^{-U/k_BT}. \tag{2.14}$$

Away from the crossover region the result goes back to the classical decay rate $(\omega_0/2\pi)e^{-U/k_BT}$.

B. Beyond steepest descent for $T<T_0^{(2)}$

Below the crossover temperature, the saddle point is named by periodic instanton or thermon. There are also two dangerous modes about this saddle point near $T_0^{(2)}$: one is the quasizero mode which is associated with a phase fluctuations of the periodic instantons with the eigenvalue and eigenstates of $\omega_2^{(b)2}=2a\varepsilon$ and $\Psi_2=\sqrt{2}\sin(\omega_b\tau)$, the other represents amplitudes fluctuation and gives large contribution to partition function with $\omega_3^{(b)2}=0$ and $\Psi_3=\sqrt{2}\cos(\omega_b\tau)$. The quasizero mode just takes the place of the ''soft mode'' which restores symmetry and the zero mode of Goldstone mode which reflects the freedom of phase. This is just the character of Global $U(1)$ symmetry broken.

Near $T_0^{(2)}$, this kind of classical periodic trajectory of thermon may be written as a Fourier series

$$x_c(\tau)=\sum_{n=0}^{\infty}[X_n\cos(\nu_n\tau)+X_{-n}\sin(\nu_n\tau)]. \quad (2.15)$$

The periodic paths near the saddle point are similar to that of Eq. (2.6): $x=x_c(\tau)+\Sigma_n Y_n\Psi_n=\Sigma_n(Y_n+X_n)\Psi_n$. We define the amplitudes into another form $Y_n'=Y_n+X_n$ and the action is

$$S[q]=\hbar\beta\Delta U+\frac{1}{2}\hbar\beta m\left[\sum_{n=-\infty,n\neq\pm1}^{\infty}\omega_n^2Y_n'^2\right]+\Delta S, \quad (2.16)$$

where

$$\Delta S=\frac{1}{2}\beta\hbar m\omega_1^{(b)2}(Y_1')^2+\frac{1}{2}\beta\hbar m\omega_{-1}^{(b)2}(Y_{-1}')^2 +B_4[(Y_1')^2+(Y_{-1}')^2]^2. \quad (2.17)$$

In terms of $Y_{\pm1}'$ we obtain the tunneling rate below $T_0^{(2)}$:

$$\Gamma=\frac{1}{\hbar\beta}\frac{\omega_0}{\omega_b}\frac{\omega_1^{(0)2}}{\Lambda}f_c[\omega_0,\omega_b]e^{-\Delta U/k_BT}, \quad (2.18)$$

where $1/\Lambda=(\kappa\sqrt{\pi}/2\omega_R^2)\mathrm{erfc}(-\kappa\varepsilon)\exp(\kappa^2\varepsilon^2)$ and $\kappa=(M\omega_R^2/2)\sqrt{(\beta/B_4)}$. In terms of κ the size of the crossover region is defined $|(T_0^{(2)}-T)/T_0^{(2)}|<1/\kappa$ in which the crossover occurs. It is obvious that there is symmetry $(T-T_0^{(2)})/T_0^{(2)}\rightarrow(T_0^{(2)}-T/T_0^{(2)})$ in the crossover region $|(T_0^{(2)}-T)/T_0^{(2)}|<1/\kappa$.

Away from the crossover region $|(T_0^{(2)}-T)/T_0^{(2)}|>1/\kappa$, the tunneling rate reduces to the standard form

$$Z_b=\frac{1}{\Delta}\frac{\sqrt{\sum_{n\neq0}\omega_n^{(0)2}}}{\sqrt{\sum_{n\neq0,1}\omega_n^{(b)2}}}e^{-S_c/\hbar}, \quad (2.19)$$

where $1/\Delta=\sqrt{(S_c/2\pi\hbar)}(\beta\hbar)$ which is known by Faddeev-Popov technique. We can reach it only through normalizing the eigenfunction of zero mode while now N may be different from the upper result for all modes being normalized: $N=(\sqrt{\omega_0^{(0)2}}\sqrt{\Sigma_{n\neq0}\omega_n^{(0)2}}/2\sinh(\beta\omega_0/2))$. The concrete parameter $\sqrt{\Sigma_{n\neq0}\omega_n^{(0)2}}/\sqrt{\Sigma_{n\neq0,1}\omega_n^{(b)2}}$ can be calculated only when $T\rightarrow T_0^{(2)}$.[23,30–32]

C. Universal law in crossover region

Beyond the steepest descent method, we have the formula Eq. (2.4) and Eq. (2.5), which is only needed in the crossover region

$$|T-T_0^{(2)}|\leqslant T_0^{(2)}/\kappa, \quad (2.20)$$

where $\kappa=(M\omega_R^2/2)\sqrt{(\beta/B_4)}\gg1$. It has been pointed out that there is a universal law in the crossover region of the second-order transition.[9,10] We use the following quantity to show the universal law:

$$y=\Gamma\exp(\Delta U/k_BT), \quad (2.21)$$

which is a function of ε but independent of the temperature T. According to the formula Eq. (2.4) and Eq. (2.5), we have the universal law in the scaling region

$$y/y_0=F(\xi/\xi_0), \quad (2.22)$$

where $F(\xi)=\mathrm{erfc}(\xi)\exp(\xi^2)$, $\xi=T-T_0^{(2)}$, $\xi_0=T_0^{(2)}/\kappa$ and $y_0=(\omega_0/2\pi)[(\omega_0^2+\omega_b^2)/2]\sqrt{(\beta\pi/6c_4}f_c[\omega_0,\omega_b]$.

III. DECAY RATE IN THE CROSSOVER REGION AT THE BOUNDARY OF SECOND-ORDER AND FIRST-ORDER TRANSITION

$B_4=0$ is the boundary of the second-order transition and the first-order one and the potential looks different from that of $B_4\neq0$: The potentials change slowly near the top and the bottom, but are rather steep in the middle. Because there is divergence of $\kappa\rightarrow\infty$ at the point of $B_4=0$, the formula (2.12) is not available.

Above $T_0^{(2)}$, the decay process arises from sphelaron $x=x_b$, too. So we have the same periodic path near the saddle point as formula (2.6). But the interactions in terms of modes differ from Eq. (2.12). We consider the sixth-order terms of the two dangerous modes

$$\Delta S=\beta\hbar\left[\begin{array}{c}\frac{M\omega_1^{(b)2}}{2}(Y_1^2+Y_{-1}^2)\\ +B_4(Y_1^2+Y_{-1}^2)^2+B_6(Y_1^2+Y_{-1}^2)^3\end{array}\right], \quad (3.1)$$

where $B_6=\frac{5}{2}c_6-(2c_4^2/M\omega_3^{(b)2})$. Near the two-phase point not only the second term $\frac{1}{2}\beta\hbar M\Sigma_{n=\pm1}\omega_n^{(b)2}Y_n^2$ tends to zero (remember here $\omega_{\pm1}^2\rightarrow0$, when temperature turns to T_c) but also B_4 is a small quantity. We consider the sixth-order terms of the two dangerous modes $B_6(Y_1^2+Y_{-1}^2)^3$. At the point $B_4=0$, there is no fourth term and the formula is reduced to

$$\frac{1}{\Lambda}=\frac{\beta}{2}[\beta B_6]^{-1/3}\int_0^{\infty}dt\exp[-(t^3-3\kappa'\varepsilon t)], \quad (3.2)$$

where $\kappa'=(\beta M\omega_b^2/3)[\beta B_6]^{-1/3}$. Below T_c, we transform Y_n to Y_n+X_n and have the same form of $1/\Lambda$.

The universal law in the crossover region $|T-T_c|\leqslant T_c/\kappa'$ is also defined as $y/y_0=F(\xi/\xi_0)$, where $F(\xi)=\int_0^{\infty}dt\exp[-(t^3+3\xi t)]$, $\xi=T-T_c$, $\xi_0=T_c/\kappa'$ and

$$y_0=\frac{\omega_0}{12\omega_b}(\omega_0^2+\omega_b^2)[\beta B_6]^{-1/3}\Gamma\left(\frac{1}{3}\right)f_c[\omega_0,\omega_b]. \quad (3.3)$$

$\Gamma(x)$ is Gamma function.

IV. THE EFFECT OF MODES OF THE FIRST-ORDER TRANSITION $B_4<0$

The actual transition occurs at the temperature when the two saddle points have the same action. For $B_4>0$ the particles tunnel through the barrier at the most *favorable* energy level $E(T)$ which goes down continuously from the top of the barrier to the bottom of the potential with lowering temperature. This corresponds to the second-order transition

from thermal activation to thermally assisted tunneling (TAT) with no discontinuity of $d\Gamma/dt$ at T_0. The transition temperature is given by $T_0^{(2)}$. For the cases of $B_4<0$, just below the top of the barrier is *unfavorable for tunneling*, the TAT mechanism is partially suppressed, and the first-order transition occurs. Because the top of the barrier is wider for $B_4<0$, the particle does not have more advantage to tunnel through the barrier from the higher excited states than the lower ones.

Let us discuss the dangerous modes near the first-order transition point: Before the eigenvalues of the two quasizero modes reach zero, the crossover occurs and the tunneling process is dominated by periodic instantons just below the top of the barrier. In this case, there is really no universal law. Above T_c which is near $\omega_R/2\pi$, the sphelaron's two dangerous modes may also play an important role on the tunneling rate at the transition point. Above the crossover temperature, the quasizero modes of sphelaron have the same eigenfunction as other cases ($B_4\geqslant 0$): $\sqrt{2}\sin(2\pi/L)\tau$ and $\sqrt{2}\cos(2\pi/L)\tau$. While there are many distinguished differences of the interaction of modes between the case of $B_4>0$ and that of $B_4<0$, the interaction between modes is attractive of the lower order terms.

After integrating the amplitudes Y_0 and Y_n, we deal with the quasizero modes to consider the fourth term

$$\frac{1}{\Lambda}=\frac{\beta}{2\pi}\int dY_1\,dY_{-1}\exp -\beta\left[\frac{1}{2}m\omega_1^{(b)2}Y_1^2+\frac{1}{2}m\omega_{-1}^{(b)2}Y_{-1}^2+B_4(Y_1^2+Y_{-1}^2)^2\right]$$
$$=\sqrt{\pi}\frac{\kappa}{2\omega_R^2}\mathrm{erfi}(-\kappa\varepsilon)\exp(\kappa^2\varepsilon^2), \tag{4.1}$$

where $\kappa=(M\omega_R^2/2)\sqrt{(\beta/B_4)}$ and $\varepsilon=[1-(T/T_0^{(2)})]$. The quasizero modes give a divergent contribution to the partition function which can be distorted into complex-plane: $\int_c^\infty \exp(x^2)dx=\int_0^\infty \exp(x^2)dx-\int_0^c \exp(x^2)dx=(i\sqrt{\pi}/2)-\mathrm{erfi}(c)$. Here $\mathrm{erfi}(c)=\int_0^c \exp(x^2)dx$. Because the real part of the function $\mathrm{erfi}(-\kappa\varepsilon)$ goes to zero as $\varepsilon\to 0$, a dramatic phenomenon arises—the first-order transition may suppress quantum tunneling rate (without considering higher-order terms)!

Because the periodic trajectories of periodic instanton cannot be written as a Fourier series if they are far below the top of the barrier, the formula (4.1) is useful only above the crossover temperature $T_0^{(1)}$.

Now we consider a *weak first-order phase transition* which is under the condition $T_0^{(1)}/T_0^{(2)}\leqslant 1-1/\kappa$. For a weak first-order phase transition, the crossover temperature $T_0^{(1)}$ is in the region $(T-T_0^{(2)})\leqslant T_0^{(2)}/\kappa$ which is shown in Fig. 1. We may define *a remaining crossover region* above the crossover temperature:

$$T_0^{(1)}\leqslant T\leqslant T_0^{(2)}+T_0^{(2)}/\kappa. \tag{4.2}$$

We also use the quantity $y=\Gamma\exp(\Delta U/k_BT)$ to show the universal law as

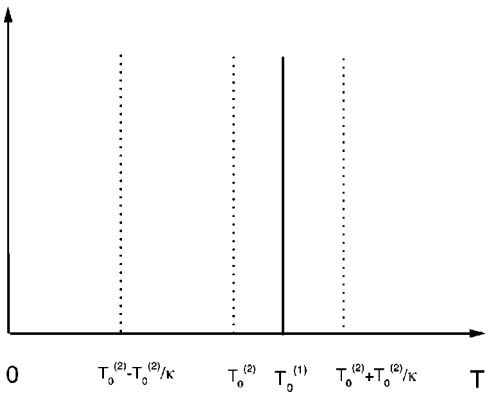

FIG. 1. The remaining scaling region of a weak first-order phase transition is $T_0^{(1)}\leqslant T\leqslant T_0^{(2)}+T_0^{(2)}/\kappa$.

$$y/y_0=F(\xi/\xi_0), \tag{4.3}$$

where $F(\xi)=\mathrm{erfi}(\xi)\exp(\xi^2)$ and $y_0=(\omega_0/2\pi)[(\omega_0^2+\omega_b^2)/2]\sqrt{(\beta\pi/6c_4)}f_c[\omega_0,\omega_b]$. For the cases $T_0^{(1)}/T_0^{(2)}>1-1/\kappa$, the first-order transition is rather sharp; there is no crossover region at all.

V. SCALING LAW OF QUANTUM CLASSICAL TRANSITION OF THE ESCAPE RATE IN $Mn_{12}Ac$

A rather simple and experimentally important system which may exhibit the first-order transition is the uniaxial spin model in a field parallel to x axis H_x described by the Hamiltonian

$$\mathcal{H}=-DS_z^2-H_xS_x \tag{5.1}$$

which is generic for problems of spin tunneling. This model is believed to be a good approximation for the molecular magnet $Mn_{12}Ac$ with D the anisotropy constant. Using the method of mapping the spin problem onto a particle problem,[23,24] we have the equivalent particle Hamiltonian as $\mathcal{H}=(p^2/2m)+U(x)$, where

$$U(x)=S^2D(h_x\cosh x-1)^2 \tag{5.2}$$

and $m=1/2D$, $h_x=H_x/2SD$, and $S\gg 1$. The minimum of the effective potential, $x_0=\cosh^{-1}(1/h_x)$, has been moved to zero. Integrating the equation of motion with imaginary time variable one obtains

$$x_p(\tau)=2\tanh^{-1}\left[\tanh x_1\,\mathrm{sn}\left(\frac{\tau-\tau_0}{\xi_P},k\right)\right] \tag{5.3}$$

$$\tanh^2 x_{1,2}=\frac{1-h_x\mp\sqrt{E'}}{1+h_x\mp\sqrt{E'}}, \tag{5.4}$$

where $\mathrm{sn}(\tau,k)$ is the Jacobi elliptic function with modulus k and the complementary modulus $k'=\sqrt{1-k^2}$, $E'=E/S^2D$. ξ_P is the characteristic length of the periodic instanton determined by the following equation:

$$\xi_P^2=\frac{1}{S^2D^2}\left(\frac{1-h_x^2}{\times\left(\dfrac{(1+k^2)h_x^2-k'^2(1-h_x^2)+h_x\sqrt{4h_x^2k^2+k'^4}}{(1+k^2)h_x^2+h_x\sqrt{4h_x^2k^2+k'^4}}\right)^2}\right)^{-1}. \tag{5.5}$$

This description corresponds to the movement of a pseudoparticle in the inverted potential $-U(x)$ with energy $-E$. The periodicity of the solution (5.3) is $\tau(E)=4\hbar\beta$, $\hbar\beta=\mathrm{K}(k)\xi_P$, where $\mathrm{K}(k)$ is the complete elliptic integral of the first kind. The Euclidean action of the periodic instanton configuration in the whole period is

$$S_p=2\int_{-\beta}^{\beta}[m\dot{x}_p^2]d\tau=W, \tag{5.6}$$

where

$$W=\frac{4}{D\xi_P\alpha^2}\{(\alpha^4-k^2)\Pi(\alpha^2,k)+k^2\mathrm{K}(k)+\alpha^2[\mathrm{K}(k)-\mathrm{E}(k)]\}, \tag{5.7}$$

where $\alpha^2=\tanh^2 x_1<k^2$ and $\mathrm{E}(k)$, $\Pi(\alpha^2,k)$ are the complete elliptic integral of second and third kind, respectively.

The period of oscillation $\tau(E)$ in the inverted potential $-U(x)$, i.e., the periodicity of the periodic instanton solution (5.3), $\tau(E)=4\mathrm{K}(k)\xi_P$, can be equivalently calculated by

$$\tau(E)=-\frac{dW(E)}{dE}=\sqrt{2m}\int_{-x_1}^{x_1}\frac{dx}{\sqrt{U(x)-E}}. \tag{5.8}$$

Near the top of the barrier, $k\to 0$,$\mathrm{K}\to\pi/2$, Eq. (5.8) yields the previously known result $\tau=2\pi/\omega_b$. Near the bottom, one has $k\to 1$, and τ logarithmically diverges. For $h_x<\frac{1}{4}$, the dependence $\tau(E)$ is nonmonotonic, and the transition is first order.

Since both S_0 and S_p are assumed to be large compared to $\hbar$, the smaller of the two determines the actual escape rate. The calculation of the temperature dependence of $S_{\min}$ is depicted in Fig. 2 for $h_x=0.1$. The solid line corresponds to the periodic instanton action S_p while the dashed one corresponds to the thermodynamic action S_0. The actual dependence of $S_{\min}(T)$ goes along the minimum of these two actions and the first-order transition occurs at $T=T_0^{(1)}$ satisfying $T_2<T_0^{(1)}<T_1$, where $k_BT_1=\hbar/\tau(E_1)$, $k_BT_2=\hbar/\tau(\Delta U)$. The first derivative of $S_{\min}(T)$ is discontinuous at $T_0^{(1)}$, providing that the crossover from the thermal to the quantum regime is the first-order transition on temperature. Quite recently an effective free energy $F=a\phi^2+b\phi^4+c\phi^6$ for the transitions of a spin system was introduced[28] as in the Landau model of second-order phase transition. Here a changes sign at the phase-transition temperature $T=T_0^{(2)}=(SD/\pi k_B)\sqrt{h_x(1-h_x)}$ and $b=0$ corresponds to the boundary between first- and second-order transitions. There indeed exists a phase boundary between the first- and second-order transitions, i.e., $h_x=\frac{1}{4}$, at which the factor in front of ϕ^2 changes the sign. At $h_x=0.3$ the minimum of F remains ΔU for all $T>T_0^{(2)}$. Below $T_0^{(2)}$ it continuously shifts from the top to the bottom of the potential as temperature is lowered. This corresponds to the second-order transition from thermal activation to TAT. At $h_x=0.1$, however, there can be one or two minima of F, depending on the temperature. The crossover between classical and quantum regimes occurs when the two minima have the same free energy, which for $h_x=0.1$ takes place at $T_0^{(1)}=1.078T_0^{(2)}$.

Near the top of the barrier the potential has the form

$$U(x)=S^2D(h_x\cosh x-1)^2=2S^2Dh_x-S^2Dh_x(h_x-1)x^2+c_4x^4+c_6x^6\ldots, \tag{5.9}$$

where $c_4=[S^2Dh_x(h_x-\frac{1}{4})/3]$ and $c_6=2S^2Dh_x(h_x-\frac{1}{24})/45$. The potentials changes slowly near the top and the bottom, but are rather steep in the middle for the cases $c_4<0$.

$h_x=\frac{1}{4}$ is the boundary of the second-order transition and the first-order one. When $h_x>\frac{1}{4}$, we have the formula Eq. [and Eq. (2.21)], which is only needed in the crossover region

$$|T-T_0^{(2)}|\leqslant T_0^{(2)}/\kappa, \tag{5.10}$$

where

$$\kappa=[h_x(1-h_x)]^{3/4}\sqrt{\frac{2\pi S}{h_x\left(h_x-\dfrac{1}{4}\right)}}\propto S^{1/2}\gg 1. \tag{5.11}$$

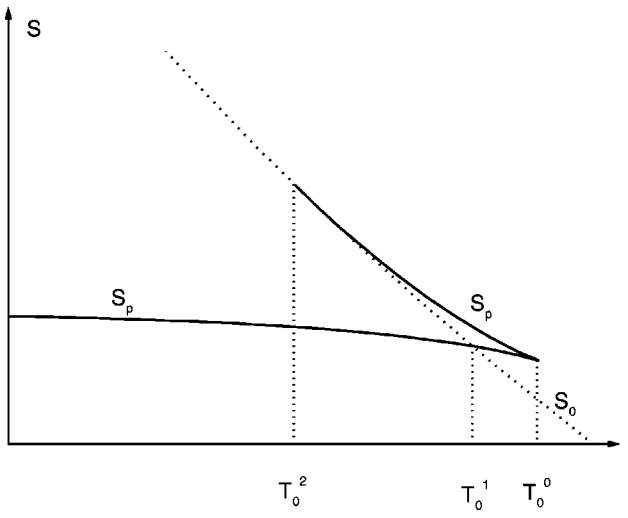

FIG. 2. First-order transition from the thermal to the quantum region for Mn_{12} molecule: $h_x=0.1$.

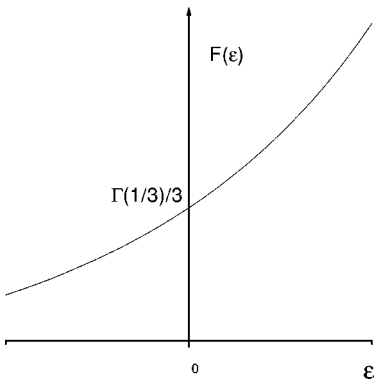

FIG. 3. Scale factor $F(\xi)$ at different sides of phase transition point of $h_x=\frac{1}{4}$.

It has been pointed out that there is a universal law in the crossover region of second-order transition.[10,11] According to the formula Eqs. (2.20) and (2.21), we have the universal law in the scaling region

$$y/y_0=F(\xi/\xi_0), \tag{5.12}$$

where $F(\xi)=\mathrm{erfc}(\xi)\exp(\xi^2)$, $\xi=T-T_0^{(2)}$, $\xi_0=T_0^{(2)}/\kappa$ and $y_0=(\omega_0/2\pi)[(\omega_0^2+\omega_b^2)/2]\sqrt{(\beta\pi/6c_4]}f_c[\omega_0,\omega_b]$.

For the case $h_x=\frac{1}{4}$, we have the crossover region $|T-T_0^{(2)}|\leqslant T_0^{(2)}/\kappa'$, where

$$\kappa'=6\left[\frac{\pi h_x(1-h_x)S}{9}\right]^{2/3}\left[h_x\left(h_x-\frac{1}{24}\right)\right]^{-1/3}\propto S^{2/3}\gg 1. \tag{5.13}$$

From the formula (3.3), we have the universal law $y/y_0=F(\xi/\xi_0)$ in the crossover region, where $F(\xi)=\int_0^\infty dt\exp[-(t^3+3\xi t)]$, $\xi=T-T_0^{(2)}$, $\xi_0=T_0^{(2)}/\kappa'$ and

$$y_0=\frac{\omega_0\beta(\omega_0^2+\omega_b^2)}{24\pi}\left[\frac{5}{2}\beta c_6\right]^{-1/3}\Gamma\left(\frac{1}{3}\right)f_c[\omega_0,\omega_b]. \tag{5.14}$$

$\Gamma(x)$ is the Gamma function which is shown in Fig. 3.

Now we consider a weak first-order phase transition which is under the condition $T_0^{(1)}/T_0^{(2)}\leqslant 1-\sqrt{[h_x(h_x-\frac{1}{4})/2\pi S][h_x(1-h_x)]^{3/4}}$. For a weak first-order phase transition, the crossover temperature $T_0^{(1)}$ is in the region $(T-T_0^{(2)})\leqslant T_0^{(2)}/\kappa$ which is shown in Fig. 1. We may define a remaining crossover region above the crossover temperature

$$T_0^{(1)}\leqslant T\leqslant T_0^{(2)}+T_0^{(2)}/\kappa. \tag{5.15}$$

We also use the quantity $y=\Gamma\exp(\Delta U/k_BT)$ to show the universal law as $y/y_0=F(\xi/\xi_0)$, where $F(\xi)=\mathrm{erfi}(\xi)\exp(\xi^2)$ and $y_0=(\omega_0/2\pi)[(\omega_0^2+\omega_b^2)/2]\sqrt{(\beta\pi/6c_4)}f_c[\omega_0,\omega_b]$. For the cases $T_0^{(1)}/T_0^{(2)}>1-\sqrt{[h_x(h_x-\frac{1}{4})/2\pi S][h_x(1-h_x)]^{3/4}}$, the first-order transition is rather sharp, there is no crossover region at all.

VI. CONCLUSION

In this paper we have shown that the decay rate Γ can accurately be determined near the crossover temperature in dissipative systems. Besides considering the WKB exponential, we have calculated contribution of the fluctuation modes around the saddle point and have given an extended account of the previous study of crossover region.[9–11] Near the phase-transition point the fluctuation modes about the saddle points include two dangerous modes whose contribution cannot be calculated by the steepest descent method and the higher-order couplings are considered between the two dangerous modes; near the point of

$$B_4=\frac{3}{2}c_4+\frac{9c_3^2}{2M\omega_b^2}-\frac{9c_3^2}{4M\omega_2^{(b)2}}=0 \tag{6.1}$$

sixth order needs to be considered. The results can be easily used in $Mn_{12}Ac$ of which the equation $B_4=[S(S+1)Dh_x(h_x-\frac{1}{4})/2]=0$ gives the phase boundary point $h_x=\frac{1}{4}$ in good agreement with earlier works.

Another example is biaxial anisotropic ferromagnetic model $\mathcal{H}=K_1S_z^2+K_2S_y^2$ which describes XOY easy plane anisotropy and an easy axis along the x direction with the anisotropy constants $K_1>K_2>0$. Mapped onto a particle problem, the equivalent particle Hamiltonian is

$$\mathcal{H}=\frac{1}{4K_1}\dot{x}^2-K_2S(S+1)\mathrm{sn}^2(x,\lambda), \tag{6.2}$$

where $\mathrm{sn}(\tau,\lambda)$ is the Jacobi elliptic function with modulus $\lambda=K_2/K_1$. From the equation $B_4=[K_2S(S+1)(1-\lambda)(1-2\lambda)/2]=0$, we obtain the phase boundary point $\lambda=\frac{1}{2}$ which confirms the results in Ref. 20.

The results of the application of a previous method[7–11] is developed for dealing with the quasizero modes and calculation of decay rate in the crossover region which is beyond the steepest descent method. The decay rate is valid for the entire interesting range of parameters in the problem of macroscopic quantum tunneling.

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