Role of an intermediate state in homogeneous nucleation

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We explore the role of an intermediate state (phase) in homogeneous nucleation by examining the decay process through a double-humped potential barrier. We analyze the one-dimensional Fokker-Planck (FP) equations with the fourth- and sixth-order Landau potentials. In the low-temperature case, we apply the WKB method to the FP equation and obtain an analytic expression for the decay rate which is accurate for a wide range of depth and curvature of the middle well. In the case of a deep middle well, it reduces to an extended Kramers formula, in which the barrier height in the original formula is replaced by the arithmetic mean height of the higher (outer) and lower (inner) barriers, and the curvature of the initial well in the original one is replaced by the geometric mean curvature of the initial and intermediate wells. In the case of a shallow middle well, the Kramers escape rate is evaluated also within the standard framework of the mean-first-passage-time problem, whose result is consistent with our WKB analysis. Criteria for enhancement of the decay rate are revealed.

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I. INTRODUCTION

Decay processes of metastable states have received considerable attention for a long time. By using the WKB analysis of the Fokker-Planck (FP) equation, van Kampen [1] investigated the role of fluctuations in thermal diffusion process in a symmetric bistable system and found that the system's ergodicity enables a Brownian particle to escape over a potential barrier. In the asymptotic time regime, he also obtained an astonishingly accurate formula for the so-called Kramers escape rate, i.e., the rate at which Brownian particles escape from a potential well over a single-humped barrier. Later, Caroli *et al.* [2] explored an asymmetric bistable system using a path integral (instanton) formalism. Matkowsky and Schuss [3] investigated the decay in metastable systems with the aid of the boundary-layer method and the saddle-point approximation around potential minima. The separation of time scales required for the Kramers rate treatment was investigated by Kapral *et al.* [4] by using the projection operator approach. For a Langevin equation with spatially and temporally correlated noise in the case of weak damping, staggered-ladder spectra of the corresponding FP equation are found [5].

Recently, Nicolis and co-workers [6,7] studied the decay in a system with a metastable intermediate state in the context of protein crystallization. Within the rate equation treatment, they gave an important suggestion that the existence of the intermediate state can enhance the nucleation rate in some parameter range. We note that the one-dimensional treatment of a chemical reaction along the reaction coordinate in the free energy landscape is very useful to describe the above problem.

In this paper, we investigate the role of an intermediate state in nucleation phenomena using the FP equation for a one-dimensional order parameter with a triple-well potential. The decay rate is given as the first excited eigenvalue of the FP operator [1,8–10,12]. As is well known, the FP equation can be transformed into the associated Schrödinger equation. Eigenvalues of the FP equation are exactly the same as those of the Schrödinger equation if there exists a well-defined thermal equilibrium in the system. In the low-temperature case, we can derive an extended Kramers formula for a double-humped potential barrier by applying the WKB approximation to the Schrödinger equation.

This paper is organized as follows. In Sec. II we reduce the FP equation to the Schrödinger equation and derive the WKB quantization condition for a system with a triple-well potential. Section III is concerned with the evaluation of the tunneling integral, which leads to the extended Kramers formula for the double-humped potential barrier. In Sec. IV the condition for the enhancement of nucleation rate caused by the intermediate state is revealed. In Sec. V we numerically check the validity of our formula for the nucleation rate. The appendix is devoted to an alternative evaluation of the nucleation rate in the case of a shallow middle well, within the standard framework of the mean-first-passage-time problem.

II. FOKKER-PLANCK EQUATION AND WKB ANALYSIS

The relaxation process responsible for homogeneous nucleation is described by the FP equation

$$\frac{\partial}{\partial t}P(x,t)=\frac{1}{\eta}\frac{\partial}{\partial x}\left(\frac{\partial W(x)}{\partial x}+\theta\frac{\partial}{\partial x}\right)P(x,t). \tag{1}$$

Here, η is the viscosity and $\theta=k_BT$ is the temperature. Hereafter we assume $\eta=1$ for simplicity, which amounts to rescaling of other parameters and variables. In order to specify the problem, we consider the symmetric triple-well potential proposed by Nicolis *et al.* [6],

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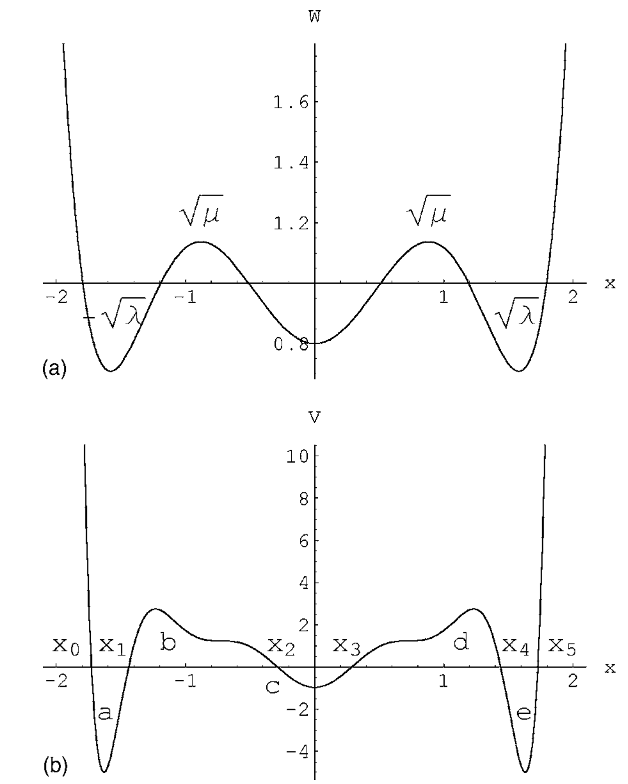

FIG. 1. (a) Landau potential $W(x)$ with $\lambda=2.5$ and $\mu=0.075$. The case of a deep middle well. (b) Corresponding effective potential $V(x)$.

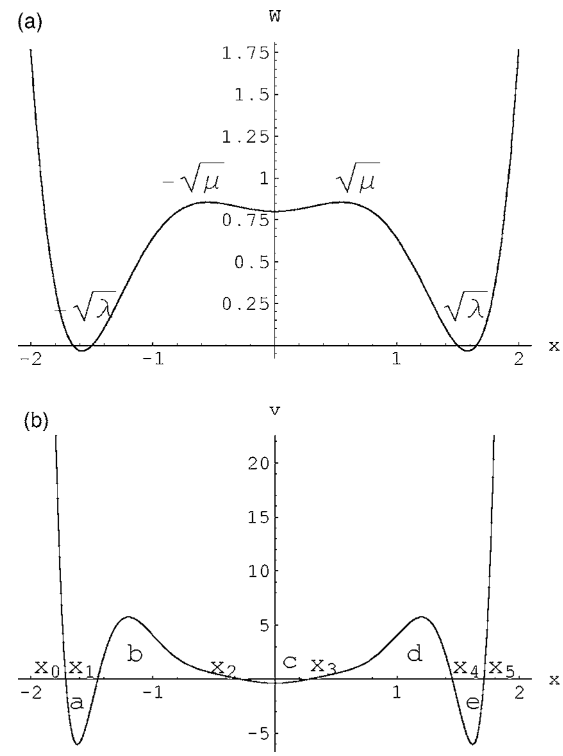

FIG. 2. (a) Landau potential $W(x)$ with $\lambda=2.5$ and $\mu=0.3$. (b) Effective potential $V(x)$ for the same parameters. Although the central well of $W(x)$ is very shallow, $V(x)$ is still negative at $x=0$, unlike the case of a double-well potential.

$$W(x) = \int dx x(x^2-\lambda)(x^2-\mu) \tag{2}$$

with $\lambda>\mu>0$, which has two global minima at $x=\pm\sqrt{\lambda}$, two local maxima at $x=\pm\sqrt{\mu}$ and one local minimum at $x=0$ as shown in Fig. 1(a). This potential represents a barrier between two stable states, which has a dip on the top corresponding to the intermediate state. By using the separation ansatz $P(x,t)=e^{-W/2\theta}\phi(x)e^{-Et}$, the FP equation is transformed into the associated Schrödinger equation

$$H\phi(x) = -\theta\phi''(x) + V(x)\phi(x) = E\phi(x). \tag{3}$$

Here, V is the effective potential

$$V(x) = \frac{W'(x)^2}{4\theta} - \frac{W''(x)}{2}, \tag{4}$$

and the temperature θ corresponds to $\hbar^2/2m$ in quantum mechanics, where $\hbar$ and m are Planck's constant and the mass, respectively. Equation (3) has the obvious lowest eigenvalue $E_0=0$ with the eigenfunction $\phi_0(x)=e^{-W/2\theta}$, and all other eigenvalues are positive. The time evolution of the probability density $P(x,t)$ is dominated by the lowest few eigenvalues of Eq. (3) except for the very early stage of relaxation. Eventually the decay rate Γ is given by the first excited eigenvalue.

As shown in Fig. 1(b), the effective potential $V(x)$ has also three wells and two barriers. It should be noted that the effective potential $V(x)$ is negative at minimum points and positive at maximum points, because $V(x)=-W''(x)/2$ if $W'(x)=0$. Therefore the effective potential $V(x)$ has three negative minima even if the middle well is very shallow, and the lowest eigenvalue $E_0=0$ is in between the three minima and the two maxima [see Figs. 1(b) and 2(b)]. Thus we are led to the tunneling problem of the three wells. We are particularly interested in the situation where, if the tunneling through the barriers is ignored, the lowest eigenvalues of the three wells are almost degenerate. Then, with the use of the WKB method, we shall remove the degeneracy by incorporating the tunneling effect and obtain the three lowest eigenvalues.

Let us denote the regions bordered by the classical turning points $x_0,\ldots,x_5$ as a, b, c, d, and e [see Fig. 1(b)]. The wave functions $\phi_a,\ldots,\phi_e$ in the respective regions are linked by the connection formula

$$\frac{1}{\sqrt{p}}e^{\pm i(S+\pi/4)} \quad (E>V) \leftrightarrow \frac{1}{\sqrt{p}}\left(e^S \pm \frac{i}{2}e^{-S}\right) \quad (E<V),$$

$$S = \left|\frac{1}{\hbar}\int_{y_0}^{x} p\,dx\right|, \quad p=\sqrt{2m|E-V(x)|}, \tag{5}$$

where y_0 denotes a classical turning point. The wave function in the leftmost region a is written as $\phi_a=(c/\sqrt{p})\sin[(1/\hbar)\int_{x_0}^{x}p\,dx+\pi/4]$, since it should not connect to a diverging term in the region $-\infty<x<x_0$. By using the connection formula, we can successively connect the wave functions to ϕ_e in the rightmost region, whose explicit form is

$$\phi_e = \frac{c}{\sqrt{p}}\left[\left(-2i\cos S_a \cos S_c e^{M_b+M_d} + \frac{i}{2}\sin S_a \sin S_c e^{-M_b+M_d} + \frac{1}{2}\cos S_a \sin S_c e^{M_b-M_d} + \frac{1}{8}\sin S_a \cos S_c e^{-M_b-M_d}\right)e^{iS_e} \times \exp\left(-\frac{i}{\hbar}\int_x^{x_5} p dx\right)e^{i\pi/4} + \left(2i\cos S_a \cos S_c e^{M_b+M_d} - \frac{i}{2}\sin S_a \sin S_c e^{-M_b+M_d} + \frac{1}{2}\cos S_a \sin S_c e^{M_b-M_d} + \frac{1}{8}\sin S_a \cos S_c e^{-M_b-M_d}\right)e^{-iS_e}\exp\left(\frac{i}{\hbar}\int_x^{x_5} p dx\right)e^{-i\pi/4}\right]. \tag{6}$$

S_α and M_β are the action and the tunneling integral in each well $\alpha=a,c,e$ and barrier $\beta=b,d$, respectively. Hereafter, wherever necessary, we use the abbreviated notation $\alpha=a,c,e$ to indicate the wells a, c, and e, respectively. Since ϕ_e in the rightmost well should not contain a term proportional to $\sin[(1/\hbar \int_x^{x_5} p\, dx - \pi/4)]$ which connects to a diverging term in the region $x_5 < x < \infty$, we obtain the following relation [10,11]:

$$4\cot S_a \cot S_c \cot S_e - \cot S_e e^{-2M_b} - \cot S_a e^{-2M_d} - \frac{1}{4}\cot S_c e^{-2(M_b+M_d)} = 0. \tag{7}$$

Due to the small transparency of the barriers, the actions are approximately quantized as $S_\alpha \approx \pi(n_\alpha + \frac{1}{2})$, and hence

$$\cot S_\alpha \approx \pi\left(n_\alpha + \frac{1}{2}\right) - S_\alpha. \tag{8}$$

Since our interest lies in the low-lying energy levels, we consider the case with $n_a=n_c=n_e=0$. In this case, for a low-lying eigenvalue E, the action is evaluated as $S_\alpha(E) \approx (E-E_\alpha)(dS/dE)|_{E=E_\alpha} + S(E_\alpha) = \pi(E-V_\alpha)/\hbar\omega_\alpha$, where E_α, $V_\alpha \equiv (E_\alpha - \hbar\omega_\alpha/2)$, and $\omega_\alpha \equiv (\pi/\hbar)[\,(dS/dE)|_{E=E_\alpha}]^{-1}$ imply the vacuum energy, (approximate) potential minimum, and frequency, respectively, defined for each well. By substituting (8) into (7), one obtains a cubic equation for the eigenvalue E:

$$4\pi^3\left(\frac{E-V_a}{\hbar\omega_a} - \frac{1}{2}\right)\left(\frac{E-V_c}{\hbar\omega_c} - \frac{1}{2}\right)\left(\frac{E-V_e}{\hbar\omega_e} - \frac{1}{2}\right) - \pi\left(\frac{E-V_a}{\hbar\omega_a} - \frac{1}{2}\right)e^{-2M_d} - \pi\left(\frac{E-V_e}{\hbar\omega_e} - \frac{1}{2}\right)e^{-2M_b} - \frac{1}{4}\pi\left(\frac{E-V_c}{\hbar\omega_c} - \frac{1}{2}\right)e^{-2(M_b+M_d)} = 0. \tag{9}$$

III. TUNNELING INTEGRALS AND DECAY RATE

The solutions of Eq. (9) constitute the lowest three eigenvalues with the lowest one being the ground state energy $E_0=0$. To reach our goal, it is necessary to evaluate the tunneling integral for each barrier. Since the potential is assumed to be symmetric, $V_a=V_e$, $M_b=M_d$, and $\omega_a=\omega_e$. The tunneling integrals can be evaluated perturbatively with use of the small parameter θ. For example, let us consider the integral on the interval $[x_3,x_4]$. As shown in Figs. 1 and 2, there is only one maximum point of the original potential W in this interval, whose coordinate is denoted by y. In this case the tunneling integral is calculated as follows. We divide the integral

$$\theta M_d = \int_{x_3}^{x_4}\sqrt{\frac{W'^2}{4} - \frac{\theta W''}{2}}dx \tag{10}$$

into three parts and perform the integration as

$$\theta M_d = \int_{x_3}^{y-\Delta}\frac{W'}{2}\left\{1 - \theta\frac{W''}{W'^2} + O(\theta^2)\right\}dx + \int_{y-\Delta}^{y+\Delta}\sqrt{\frac{-\theta W''}{2}} \times\left\{1 - \frac{W'^2}{4\theta W''} + O\left(\left(-\frac{W'^2}{2\theta W''}\right)^2\right)\right\}dx - \int_{y+\Delta}^{x_4}\frac{W'}{2} \times\left\{1 - \theta\frac{W''}{W'^2} + O(\theta^2)\right\}dx = -\frac{W(x_3)+W(x_4)}{2} + W(y) - \theta\ln[-W''(y)\sqrt{\theta}] + O(\theta). \tag{11}$$

We choose $\Delta=\sqrt{|2\theta/W''(y)|}$ so that the Taylor expansion $\sqrt{1+x}=1+x/2+O(x^2)$ is possible in the calculation above.

Equation (9) is solved as follows. When the barrier heights are large enough, exponentially small tunneling factors are negligible on the left-hand side of (9), giving a set of the lowest eigenvalues at each of the separate wells, $E_{a,e}=\hbar\omega_a/2+V_a$ and $E_c=\hbar\omega_c/2+V_c$. If the tunneling effect is incorporated, these three levels split (see Figs. 3 and 4). In such a case one can still ignore the fourth term on the left-hand side of (9), because it contains a product of two small tunneling terms. Then one obtains the eigenvalues

$$E_a = \frac{\hbar\omega_a}{2} + V_a,$$

$$E_\pm = \frac{\hbar\omega_a/2 + V_a + \hbar\omega_c/2 + V_c}{2} \pm \frac{1}{2}\sqrt{\left\{\left(\frac{\hbar\omega_a}{2} + V_a\right) - \left(\frac{\hbar\omega_c}{2} + V_c\right)\right\}^2 + \frac{2\hbar^2\omega_a\omega_c}{\pi^2}e^{-2M_d}}, \tag{12}$$

where E_- stands for $E_0=0$. The decay rate is given as the difference of the two low-lying eigenvalues $\Gamma = E_a - E_-$.

Depending on the depth of the middle well of $V(x)$, there are two typical cases:

case (a):

$$\left|\left(\frac{\hbar\omega_a}{2} + V_a\right) - \left(\frac{\hbar\omega_c}{2} + V_c\right)\right| \ll \frac{\sqrt{2}\hbar\sqrt{\omega_a\omega_c}}{\pi}e^{-M_d};$$

case (b):

$$\left|\left(\frac{\hbar\omega_a}{2} + V_a\right) - \left(\frac{\hbar\omega_c}{2} + V_c\right)\right| \gg \frac{\sqrt{2}\hbar\sqrt{\omega_a\omega_c}}{\pi}e^{-M_d}.$$

The cases (a) and (b) correspond to deep and shallow middle wells, respectively. The energy splitting and shifts in each of these cases are illustrated in Figs. 3 and 4. Our principal interest lies in the case (a) where the unperturbed three levels without tunneling effect are almost degenerate. In this case the first term in the square root in Eq. (12) is negligible and the decay rate is dominated by the tunneling term. Then we obtain

$$\Gamma = E_a - E_- = \sqrt{\frac{4\hbar^2\omega_a\omega_c\theta|W''(y)|}{\pi^2|W'(x_4)W'(x_3)|}} \times e^{1-\sqrt{2}-\mathrm{arcsinh}(1)}e^{-[W(y)-W(x_3)+W(y)-W(x_4)]/2\theta} \tag{13}$$

with the turning points $x_3=\sqrt{2\theta/\lambda\mu}$, $x_4=\sqrt{\lambda}-\sqrt{\theta/\lambda(\lambda-\mu)}$ and the maximum point $y=\sqrt{\mu}$ in the tunneling integral.

Using the harmonic approximation $\hbar\omega_{a,c,e} \approx \sqrt{2\theta V''(x^{min}_{a,c,e})}$ for the curvature of each well of $V(x)$, (13) is rewritten in the lowest order of θ as

$$\Gamma = \frac{\sqrt{2}-1}{\pi}e^{2-\sqrt{2}}\sqrt{2\sqrt{W''(0)W''(\sqrt{\lambda})}|W''(\sqrt{\mu})|}e^{-(\Delta U_1+\Delta U_2)/2\theta}, \tag{14}$$

where $\Delta U_1 = W(\sqrt{\mu}) - W(\sqrt{\lambda})$ and $\Delta U_2 = W(\sqrt{\mu}) - W(0)$ are the height of the potential barrier measured from the bottoms of the left well and the middle well, respectively. $W''(0)$, $W''(\sqrt{\mu})$, and $W''(\sqrt{\lambda})$ are the curvatures at the middle well, at the barrier top, and at the bottom of the left well, respectively. These quantities are illustrated in Fig. 5. In deriving (14) from (13) we used the expressions $\sqrt{2\theta V''(x_{a,e})} = W''(\sqrt{\lambda})$, $\sqrt{2\theta V''(x_c)} = W''(0)$, $W'(x_3) = \sqrt{2\theta W''(0)}$, and $W'(x_4) = \sqrt{2\theta W''(\sqrt{\lambda})}$, which are valid in the lowest order of θ.

Equation (14) is a double-humped-barrier counterpart of the Kramers escape rate for a single barrier, since the potential-barrier height and the curvature of the initial well in the Kramers rate are replaced by the arithmetic mean height of the higher (outer) and lower (inner) partial barriers (ΔU_1 and ΔU_2) and the geometric mean curvature of the initial and intermediate wells [$W''(\sqrt{\lambda})$ and $W''(0)$], respectively (see Fig. 5). Equation (14) cannot be obtained within the standard framework of the mean-first-passage-time problem.

On the other hand, in the case (b), one can Taylor-expand the formula in Eq. (12) with respect to the small tunneling term, finding

$$E_- = E_a - \frac{1}{2\left|\left(\frac{\hbar\omega_a}{2} + V_a\right) - \left(\frac{\hbar\omega_c}{2} + V_c\right)\right|}\frac{\hbar^2\omega_a\omega_c}{\pi^2}e^{-2M_d}.$$

In this case the decay rate is given by

$$\Gamma = E_a - E_- = \frac{(\sqrt{2}-1)^2}{\pi^2}e^{4-2\sqrt{2}}\frac{2\sqrt{W''(0)W''(\sqrt{\lambda})}|W''(\sqrt{\mu})|}{|(\hbar\omega_a/2+V_a)-(\hbar\omega_c/2+V_c)|} \times e^{-(\Delta U_1+\Delta U_2)/\theta}. \tag{15}$$

Although in this case the difference of the unperturbed energy levels $(\hbar\omega_a/2+V_a)-(\hbar\omega_c/2+V_c)$ cannot be written simply in terms of the original potential, the activation energy $\Delta U_1 + \Delta U_2$ with $\Delta U_2 \approx 0$ is nearly equal to the barrier height measured from the bottom of the left well. Thus the conventional Kramers escape rate is recovered in this case. As is proved in the Appendix, the result in Eq. (15) can be confirmed by an alternative derivation of the decay rate within the standard framework of the mean-first-passage-time problem.

IV. ENHANCEMENT OF NUCLEATION RATE

We proceed to investigate the possibility of enhancement of nucleation due to the existence of an intermediate state on the basis of the low-temperature formula for the double-humped-barrier version of the Kramers rate.

In the case of a symmetric double-well potential $W(x) = x^4/4 - \nu x^2/2$ in Fig. 6, the decay rate is calculated [1] in the same way as in the previous section and is given by

$$\Gamma' = \frac{\sqrt{2}-1}{\pi}\sqrt{W''(\sqrt{\nu})|W''(0)|}e^{2-\sqrt{2}}e^{-\Delta U/\theta} \tag{16}$$

with the barrier height $\Delta U = W(0) - W(\sqrt{\nu})$ (see Fig. 6). We note that a faster decay due to the existence of an interme-

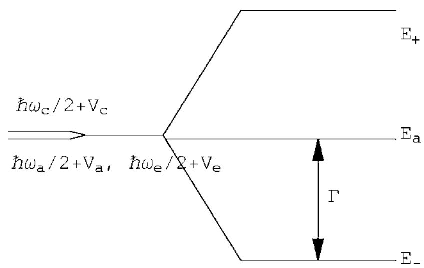

FIG. 3. Energy splitting and shifts in the case (a) of a deep middle well. The unperturbed three eigenvalues are almost degenerate.

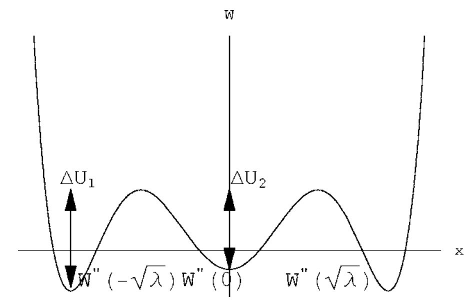

FIG. 5. The potential barriers ΔU_1 and ΔU_2 and the curvatures in the original potential $W(x)$.

diate state is guaranteed under the following conditions: (i) The Boltzmann factor for the double-humped barriers is larger than that for the single barrier; (ii) the two Boltzmann factors are identical, and the preexponential factor for the double-humped barriers is larger than that for the single barrier.

The condition (i) implies that the mean barrier height $(\Delta U_1+\Delta U_2)/2$ for the triple-well potential is less than the barrier height ΔU for the double-well potential. To be more explicit, the condition (i) is given by

$$\nu > \sqrt{G(\lambda,\mu)}, \quad G(\lambda,\mu) \equiv \frac{\lambda^3 - 3\lambda^2\mu + 6\lambda\mu^2 - 2\mu^2}{6}. \tag{17}$$

On the other hand, in the case (ii) the condition for the Boltzmann factors $(\Delta U_1+\Delta U_2)/2=\Delta U$ leads to

$$\nu = \sqrt{G(\lambda,\mu)}; \tag{18}$$

namely, ν is a function of λ and μ. For the preexponential factors to satisfy $\Gamma > \Gamma'$, we have

$$\lambda\mu^{3/2}(\lambda-\mu)^{3/2} > 2^{-3/2}\nu^2. \tag{19}$$

The condition (ii) is given by Eqs. (18) and (19) in our model.

In the same way, enhancement of the nucleation due to the intermediate state is also expected in the case of the sixth-order double-well Landau potential $W(x)=x^6/6-(\kappa/4)x^4$. For instance, the condition (i) is now given by

$$\kappa > [3G(\lambda,\mu)]^{1/3}. \tag{20}$$

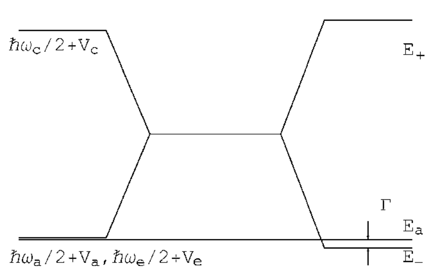

FIG. 4. Energy splitting and shifts in the case (b) of a shallow middle well. The unperturbed eigenvalue for the central well is separated from the doubly degenerate ones in the left and right wells.

V. NUMERICAL EVALUATION OF THE DECAY RATE

To verify the results in the previous sections, we shall investigate the decay rate numerically by calculating the second lowest eigenvalue of the associated Schrödinger operator $H=p^2/2+V(x)$ in Eq. (3) [13,14]. Since the potential $V(x)$ is a polynomial in our model, a matrix representation of the Hamiltonian with respect to the harmonic oscillator basis is obtained analytically with use of the annihilation-creation operator representation of p and x. Then the matrix is truncated and diagonalized numerically [15].

For the system with a triple-well potential, the decay rate is obtained numerically in the parameter range $\theta=0.1$, $2<\lambda<3$, $0.3<\mu<1$, which is compared with Eq. (14) in the case of a deep middle well (Fig. 7). In Fig. 7(a), there certainly exists a region (hereafter referred to as the "coincidence region") where the decay rates Γ in both the numerical and analytical results [Eq. (14)] coincide [see Fig. 7(a)]. The best agreement can be seen along the "coincidence line," on which the unperturbed ground energies (in the harmonic approximation) of the three wells are exactly the same. In the vicinity of the coincidence region, the curvatures of the left and middle wells are almost the same in the original Landau potential $W(x)$, and the unperturbed eigenvalues of the three wells in the effective potential $V(x)$ are almost degenerate, satisfying the condition for the case (a). Thus we see that the double-humped-barrier counterpart of the Kramers formula can be justified near the coincidence line [see Fig. 7(b)] in the present context.

In the case of a shallow central well, which lies far from the coincidence region, the degeneracy condition is no longer

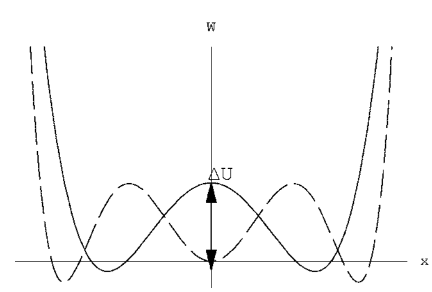

FIG. 6. Schematic picture of the symmetric double-well potential $W(x)$ with (broken line) and without (solid line) a dip on the barrier. ΔU is the barrier height in the case of the double-well potential with no dip on the barrier.

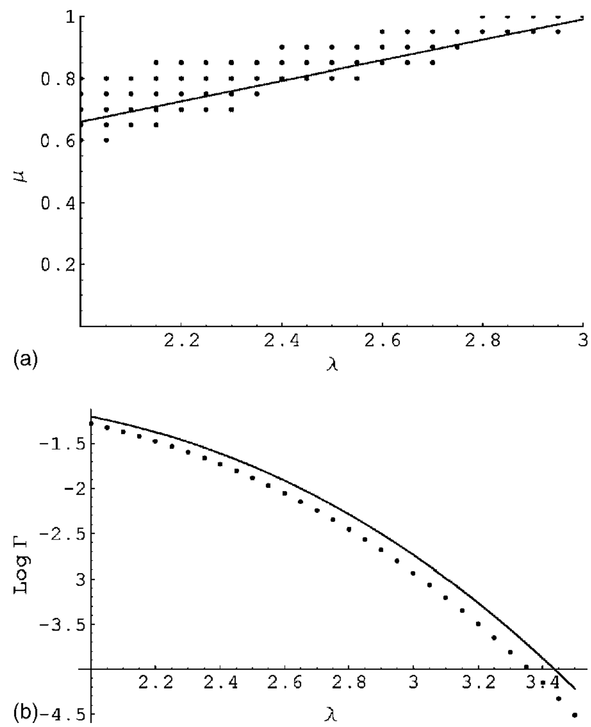

FIG. 7. Comparison of the decay rate Γ between the analytic formula in Eq. (14) and numerically obtained values (dots) in the parameter range $2<\lambda<3$, $0.3<\mu<1$, at $\theta=0.1$. (a) Coincidence region where the ratio of the numerical and analytical decay rates falls between 0.819 and 1.221. Along the coincidence line (solid line), the symmetric level splitting is observed as depicted in Fig. 3. (b) Comparison between numerical (dots) and analytical (solid line) decay rates along the coincidence line in (a).

satisfied. At $\lambda=3$, $\mu=0.3$, for instance, the middle well is astonishingly shallow. Here, instead of Eq. (14), Eq. (15) explains the numerical Boltzmann factor. In the Appendix we derive the double-humped-barrier counterpart of the Kramers rate as the inverse of the first passage time. Due to the saddle-point approximation, however, this method is valid only in the case of a shallow central well.

VI. SUMMARY AND DISCUSSIONS

With use of the WKB method, we have analyzed the homogeneous nucleation phenomena in systems with an intermediate state, and obtained the decay rate for the thermal diffusion over a double-humped barrier. The analytic result is applicable for a wide range of depth and curvature of the intermediate middle well. In the case of a deep middle well, in particular, our result becomes an extended Kramers escape rate for the double-humped barrier: the barrier height and the curvature of the initial well in the Kramers rate are now replaced by the arithmetic mean height of the higher and lower partial barriers and the geometric mean curvature of the initial and intermediate wells, respectively. We have confirmed the presence of the coincidence region in the parameter space of the Landau potential, where our formula holds well. We have also revealed the condition for the intermediate state to enhance the nucleation rate. In the case of a

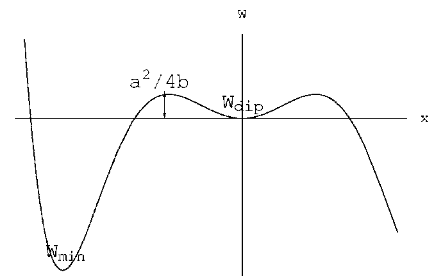

FIG. 8. Schematic picture of the double-humped potential $W(x)$ with a shallow middle well.

shallow middle well, which is far from the coincidence parameter region, we find a less essential modification of the Kramers rate, which is also verified by another calculation based on the standard framework of the mean-first-passage-time problem.

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APPENDIX: METHOD OF THE MEAN-FIRST-PASSAGE TIME: THE CASE OF A SHALLOW MIDDLE WELL

For a double-humped-barrier potential W with a shallow middle well (Fig. 8), the counterpart of the Kramers escape rate is straightforwardly derived with the aid of the saddle-point approximation for the mean-first-passage time [16,17]. The left well is approximated as a harmonic potential and the middle well is described by a fourth-order symmetric potential $(a/2)x^2-(b/4)x^4$. The mean first passage time $\tau(x)$ from an initial point x is given by

$$\tau(x)=\eta\int_x^{x_a}dy\, e^{W(y)/\theta}\int_{-\infty}^{y}dz\, e^{-W(z)/\theta}, \tag{A1}$$

where the boundary x_a is larger than the two potential maximum points. We further assume that a Brownian particle can not come back once it leaves the domain $[-\infty,x_a]$. At low temperature, the saddle-point approximation for the integral over z gives

$$\int_{-\infty}^{y}dz\, e^{-W(z)/\theta}\approx\int_{-\infty}^{\infty}dz\, e^{-W(z)/\theta}=e^{-W_{min}/\theta}\sqrt{\frac{2\pi\theta}{\omega_{min}^2}}. \tag{A2}$$

Here W_{min} and ω_{min} are the potential minimum and the curvature at the minimum point x_{min} in the left well.

The integration over y is performed as

$$\int_x^{x_a} dy\, e^{W(y)/\theta} \approx \int_{-\infty}^{\infty} dy \exp\left(\frac{W_{dip} - (a/2)y^2 + (b/4)y^4}{\theta}\right) = \frac{\pi}{2}\sqrt{\frac{a}{b}} e^{(W_{dip}+a^2/8b)/\theta}\left\{ I_{-1/4}\left(\frac{a^2}{8b\theta}\right) + I_{1/4}\left(\frac{a^2}{8b\theta}\right)\right\} \tag{A3}$$

with W_{dip} being the potential minimum in the dip. The decay rate Γ is given by the inverse of τ as

$$\Gamma = \frac{2\omega_{min}}{\pi\sqrt{2\pi\theta a/b}} e^{-(W_{dip}-W_{min}+a^2/8b)/\theta}\left\{ I_{-1/4}\left(\frac{a^2}{8b\theta}\right) + I_{1/4}\left(\frac{a^2}{8b\theta}\right)\right\}^{-1}. \tag{A4}$$

At low temperature, with use of the asymptotic form for the modified Bessel function $I_k(z) \sim e^z/\sqrt{2\pi z}$, Eq. (A4) turns out to be the usual Kramers escape rate

$$\Gamma = \frac{\sqrt{a}\,\omega_{min}}{2\pi} e^{-\Delta W/\theta}, \tag{A5}$$

where $\Delta W = W_{dip} - W_{min} + a^2/4b$ stands for the net barrier height measured from the bottom of the left well, and $\sqrt{a}$ corresponds to the curvature at the top. Equation (A5) is nothing but the decay rate for the limiting case of a shallow middle well, and accords with Eq. (15). We note that in [3], the Kramers rate is derived with the aid of combined application of the boundary-layer method with the harmonic approximation of potential maxima and the saddle point approximation for each minima. Consequently their analysis is applicable to a limited region in the parameter space such as the case of a shallow middle well, leading to the same issue as (A5). Thus we see that the effect of the intermediate state is not fully incorporated in this formalism.

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