# Nucleation rate of critical droplets on an elastic string in a $\phi^6$ potential

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We obtain the nucleation rate of critical droplets for an elastic string moving in a $\phi^6$ local potential and subject to noise and damping forces. The critical droplet is a bound soliton-antisoliton pair that carries a section of the string out of the metastable central minimum into one of the stable side minima. The frequencies of small oscillations about the critical droplet are obtained from a Heun equation. We solve the Fokker-Planck equation for the phase-space probability density by projecting it onto the eigenfunction basis obtained from the Heun equation. We employ Farkas' "flux-overpopulation" method to obtain boundary conditions for solving the Fokker-Planck equation; these restrict the validity of our solution to the moderate to heavy damping regime. We present results for the rate as a function of temperature, well depth, and damping.

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## I. INTRODUCTION

"The problem of escape from metastable states is ubiquitous in almost all scientific areas." This felicitous characterization of the importance and range of applicability of reaction rate theory begins an authoritative review [1] of the development of the subject, up to 1990. Since the presentation in this review is so complete, we refer the reader to it for the details of this development. Additional papers relevant to the subject, which were published after Ref. [1] was completed, are mentioned below.

The present paper is a contribution to the calculation of reaction rates for a one-dimensional continuum system—i.e., an elastic string moving in a external local potential energy and subject to damping and noise forces arising from coupling to a heat bath. This particular application of nucleation theory was initiated by Seeger and Schiller [2] and by Hirth and Lothe [3], and has had important contributions from others [4–6]. For these authors, the experimental impetus came from observations of dislocation motion in crystals. In this approach, the dislocation moves through the crystal by nucleation of bound soliton-antisoliton pairs in its displacement field.

In a previous paper [7], we outlined a calculation of the soliton-antisoliton nucleation rate for a string moving in an asymmetric double-well $\phi^4$ potential. In general such rate calculations require calculating the frequency spectrum of small oscillations about the "critical droplet" (the soliton-antisoliton pair). For this system we showed how this calculation reduced to solving a Heun equation, a particular generalization of the hypergeometric equation that was introduced in 1889 [8]. In recent years this equation has been found useful to solve several problems of physical interest [9–12].

In the present paper we extend these calculations to a string moving in a symmetric triple-well local potential energy, the so-called $\phi^6$ potential, restricted to the situation where the right and left side wells are deeper than the center well. There is a bound soliton-antisoliton solution to the equations of motion, which lies mostly in the center well but which makes a single excursion into one of the side wells. That solution is the critical droplet for nucleation of the string out of the metastable central well into one of the stable side wells. The calculation of the spectrum of small oscillations about this critical droplet again reduces to solving a Heun equation, and we provide the details of that calculation here.

The calculations here are restricted to the case of moderate to large damping. Different methods are required to treat the case of weak damping [13].

To our knowledge there has not been a calculation of the nucleation rate for a continuum system with the $\phi^6$ local potential energy. There has been one paper that treats a single particle moving in a triple-well potential, with emphasis on the whole range of damping (the "Kramers' turnover problem") [14].

The outline of this paper is as follows. In Sec. II we describe our system, give the critical droplet solution of its equation of motion, and formulate the problem of small oscillations about the critical droplet. In Sec. III we relate the small oscillation problem to the Heun equation and calculate the spectrum of small oscillations about the critical droplet. In Sec. IV, we describe our Fokker-Planck equation, taking care that we include the whole phase space of our continuum system. In Sec. V, we solve the Fokker-Planck equation for the phase-space probability distribution function with appropriate boundary conditions, and in Sec. VI we use it to calculate the flow of probability flux over the saddle point on the energy surface in phase space. This last calculation gives the nucleation rate. We give the results of numerical evaluations of our formula for the nucleation rate in Sec. VII, and we give our conclusions in Sec. VIII. Some technical parts of our calculations are given in the Appendixes.

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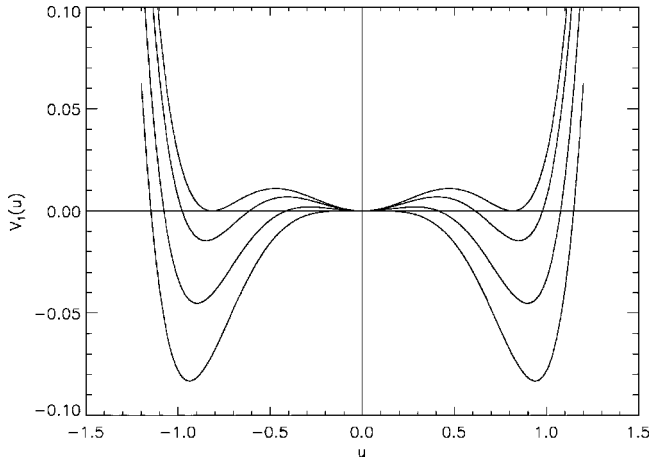


FIG. 1. The local potential $V_1(u)$. From bottom to top the values of the shape parameter $a$ are 0.01, 0.1, 0.18, 0.22222.

## II. SYSTEM

We consider a one-dimensional system consisting of an elastic string moving in an external potential energy. The Hamiltonian, a functional of the momentum density field $\pi(x,t)$ and the displacement field $u(x,t)$, is

$$H[\pi,u]=\int_{-\infty}^{\infty}dx\left[\frac{1}{2}\pi^2+\frac{1}{2}c_0^2\left(\frac{\partial u}{\partial x}\right)^2+V_1(u)\right], \quad (2.1)$$

where $c_0$ is a constant and the local potential is the symmetric function

$$V_1(u)=\tfrac{1}{2}au^2-\tfrac{1}{3}u^4+\tfrac{1}{4}u^6,\ 0<a<2/9 \quad (2.2)$$

(see Fig. 1). (All quantities here are dimensionless. The scaling factors used to achieve this form are given in Appendix A.) For values of the "shape parameter" $a$ in the range $0<a<2/9$, $V_1(u)$ has a double root at $u=0$ and four other roots at

$$u=\pm\left[\frac{2}{3}\pm\sqrt{2\left(\frac{2}{9}-a\right)}\right]^{1/2}. \quad (2.3)$$

$V_1(u)$ has a metastable minimum at

$$u_{ms}=0, \quad (2.4)$$

stable minima at

$$\pm u_s=\pm\left[\frac{4}{9}+\sqrt{\frac{2}{3}\left(\frac{8}{27}-a\right)}\right]^{1/2}, \quad (2.5)$$

and maxima at

$$\pm u_{max}=\pm\left[\frac{4}{9}-\sqrt{\frac{2}{3}\left(\frac{8}{27}-a\right)}\right]^{1/2}. \quad (2.6)$$

For $0<a<2/9$, $V_1(\pm u_s)<V_1(u_{ms})$, and at $a=2/9$, the three minima become degenerate, $V_1(\pm u_s)=V_1(u_{ms})$.

The deterministic Hamiltonian equations of motion (EOM) obtained from Eq. (2.1) are

$$\frac{\partial u(x,t)}{\partial t}=\frac{\delta H}{\delta\pi(x)}=\pi(x,t), \quad (2.7)$$

$$\frac{\partial\pi(x,t)}{\partial t}=-\frac{\delta H}{\delta u(x)}=c_0^2\frac{\partial^2 u}{\partial x^2}-V_1'(u)=c_0^2\frac{\partial^2 u}{\partial x^2}-au+\frac{4}{3}u^3-\frac{3}{2}u^5. \quad (2.8)$$

Extremal points on the energy surface (in phase space) are solutions of the equations

$$\frac{\delta H}{\delta\pi(x)}=0=\pi(x),\ \frac{\delta H}{\delta u(x)}=0=-c_0^2u_{xx}+V_1'(u(x)). \quad (2.9)$$

Equations (2.7)–(2.9) imply that extremal solutions are static. Two trivial solutions of Eqs. (2.9) are the metastable solution

$$\pi_{ms}(x)\equiv 0,\ u_{ms}(x)\equiv u_{ms}=0 \quad (2.10)$$

and the stable solution

$$\pi_s(x)\equiv 0,\ u_s(x)\equiv u_s. \quad (2.11)$$

We look for additional solutions of Eqs. (2.9) that have the string lying in the upper (metastable) well of $V_1(u)$ for most of the range of $x$, but also have an interval of the string making a smooth transition over the barrier separating the metastable well from one of the stable wells and back. These are solutions that describe a configuration of the string "…which is everywhere the same as the initial metastable state except for the presence of a single localized fluctuation, e.g., a droplet" [15]. [Of course for the $V_1(u)$ in Eq. (2.2) there are two, symmetric, solutions going into either the right or left stable well; for definiteness, we choose the solution with $u(x)>0$.] Thus the boundary conditions to be imposed are that $u$ and its first derivative vanish at $\pm\infty$, corresponding to most of the chain lying in the metastable minimum. In Appendix B we find such a spatially nonuniform extremal solution, the "critical droplet" [15] or "bounce" [16],

$$\pi_b(x)\equiv 0, \quad (2.12)$$

$$u_b(x)=\sqrt{\frac{3a}{1+\frac{3}{\sqrt{2}}\sqrt{\frac{2}{9}-a}\cosh\left(\frac{2\sqrt{a}}{c_0}x\right)}} \quad (2.13)$$

$$=\sqrt{\sqrt{\frac{a}{2}}\left\{\tanh\left[\frac{\sqrt{a}}{c_0}(x+x_0)\right]-\tanh\left[\frac{\sqrt{a}}{c_0}(x-x_0)\right]\right\}}. \quad (2.14)$$

Equation (2.14) shows that the bounce is a soliton-antisoliton bound pair [17] whose centers are separated by

$$2x_0=\frac{c_0}{2\sqrt{a}}\ln\left[\frac{\sqrt{2}/3+\sqrt{a}}{\sqrt{2}/3-\sqrt{a}}\right], \quad (2.15)$$

which diverges logarithmically when $a\to 2/9$. The maximum value of $u_b(x)$ is the smaller root of $V_1(u)$, given in Eq. (2.3) [cf. Eq. (B2) for $K=2$] and increases with increasing $a$.

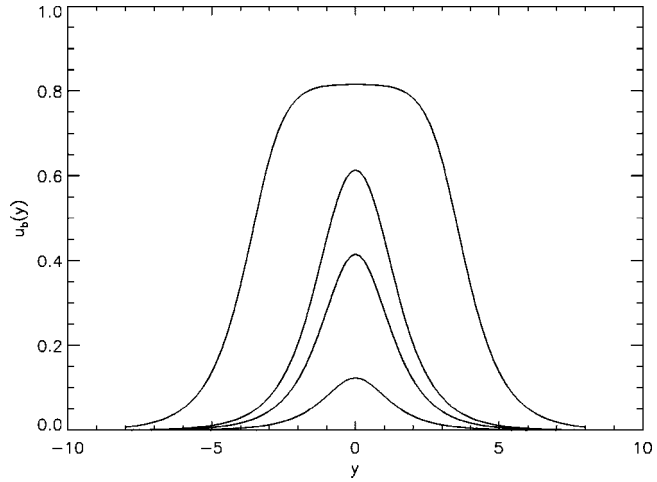


FIG. 2. From bottom to top along the ordinate, the bounce solution for $a=0.01$, 0.1, 0.18, 0.2222. The independent variable is $y=\sqrt{a}x/c_0$.

In writing Eqs. (2.13) and (2.14), we have chosen to center the bounce at the origin; it could be anywhere. Plots of $u_b(x)$ for several values of $a$ are in Fig. 2.

The energy of the bounce is obtained by using Eq. (2.13) in Eq. (2.1) and evaluating the integral. The result is

$$E_b = c_0\left\{\frac{\sqrt{a}}{3} + \frac{1}{2\sqrt{2}}\left(\frac{2}{9} - a\right)\ln\left[\frac{\sqrt{2}/3 - \sqrt{a}}{\sqrt{2}/3 + \sqrt{a}}\right]\right\}. \quad (2.16)$$

It rises monotonically from $E_b(a=0)=0$ to $E_b(a=2/9)=c_0\sqrt{2}/9$. A condition for the validity of the statistical-mechanical calculations presented in this paper is that the temperature $T$ should satisfy $k_BT \ll E_b$. This condition ensures that the notion of metastability makes sense. It becomes quite restrictive of the temperature range for $a\to 0$ because $E_b\to 0$ there. We can expect that this theory is not valid for small $a$ because quantum effects become important at low temperature.

From Eq. (2.9) we calculate the functional second derivatives of the energy to be

$$\frac{\delta^2 H}{\delta\pi(x)\,\delta\pi(x')} = \delta(x-x'), \quad (2.17)$$

$$\frac{\delta^2 H}{\delta u(x)\,\delta\pi(x')} = 0, \quad (2.18)$$

$$\frac{\delta^2 H}{\delta u(x)\,\delta u(x')} = \left[-c_0^2\frac{\partial^2}{\partial x^2} + V_1''(u)\right]\delta(x-x'). \quad (2.19)$$

Because of Eqs. (2.9) and (2.18), for small fluctuations $\delta\pi(x,t)$ and $\delta u(x,t)$ about the bounce $(\pi_b(x), u_b(x))$ the energy is

$$H = E_b + \frac{1}{2}\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dx'\left[\left(\frac{\delta^2 H}{\delta\pi(x)\,\delta\pi(x')}\right)_b \delta\pi(x)\,\delta\pi(x') + \frac{1}{2}\left(\frac{\delta^2 H}{\delta u(x)\,\delta u(x')}\right)_b \delta u(x)\,\delta u(x')\right] + \cdots, \quad (2.20)$$

where the functional derivatives are evaluated at the bounce. To simplify this expression we introduce the eigenfunctions $\phi_n(x)$ and eigenvalues $\omega_n^2$ of $(\delta^2 H/\delta u(x)\,\delta u(x'))_b$, which are solutions of

$$\int_{-\infty}^{\infty}dx'\left(\frac{\delta^2 H}{\delta u(x)\,\delta u(x')}\right)_b \phi_n(x') = \omega_n^2\phi(x). \quad (2.21)$$

We use Eq. (2.19) in Eq. (2.21) and find that this eigenvalue equation is the differential equation

$$\begin{aligned} -c_0^2\frac{d^2\phi_n}{dx^2} + V_1''(u_b(x))\,\phi_n &= -c_0^2\frac{d^2\phi_n}{dx^2} + \left[a - 4u_b^2(x) + \frac{15}{2}u_b^4(x)\right]\phi_n(x) \\ &= \omega_n^2\phi_n(x). \end{aligned} \quad (2.22)$$

Since this is a Schrödinger equation, the set of eigenfunctions $\{\phi_n\}$ is a complete orthonormal set, and we use it to express the small oscillations about the bounce as

$$\delta u(x,t) = \sum_n \zeta_n(t)\,\phi_n(x), \quad (2.23)$$

$$\delta\pi(x,t) = \sum_n \xi_n(t)\,\phi_n(x). \quad (2.24)$$

Finally, we use Eqs. (2.17), (2.20), (2.21), (2.23), and (2.24) to write the energy for small fluctuations about the bounce as

$$H = E_b + \frac{1}{2}\sum_n \xi_n^2 + \frac{1}{2}\sum_n \omega_n^2\zeta_n^2 + \cdots. \quad (2.25)$$

In Eqs. (2.21)–(2.25) $n$ denotes a generic eigenfunction label and the sums are over the complete set of eigenfunctions. The eigenvalues $\omega_n^2$ and corresponding eigenfunctions $\phi_n$ in Eqs. (2.21) and (2.22) are calculated in Sec. III.

The Hamiltonian can also be expanded for small oscillations about the metastable solution, Eq. (2.10). The expansion looks like Eq. (2.20) except that the energy of the metastable solution is zero and the $b$ subscripts are replaced by $ms$ subscripts. Instead of Eq. (2.22), the eigenvalue equation is

$$-c_0^2\frac{d^2\phi_n^{(ms)}}{dx^2} + a\,\phi_n^{(ms)} = \omega_{ms,n}^2\phi_n^{(ms)} \quad (2.26)$$

and the expansion of the energy near the metastable solution is

$$H = \frac{1}{2}\sum_n \xi_{ms,n}^2 + \frac{1}{2}\sum_n \omega_{ms,n}^2\zeta_{ms,n}^2 + \cdots. \quad (2.27)$$

The partition function determined by this quadratic Hamiltonian will be needed in Sec. VI.

## III. SMALL OSCILLATIONS AROUND THE CRITICAL DROPLET

In this section we describe the solution of the linear eigenvalue equation for the small oscillations about the bounce, Eq. (2.22), as a function of the shape parameter $a$. Since Eq. (2.22) is a one-dimensional Schrödinger equation, all the knowledge developed to solve this equation for quantum systems is applicable here. For example, the "potential energy" in Eq. (2.22) is an even function of $x$, since $u_b(x)$ [Eq. (2.14)] is an even function of $x$. Therefore, nondegenerate solutions of Eq. (2.22) have definite parity, and degenerate solutions can be chosen to have definite parity.

### A. Stability of the bounce

Equations (2.7) and (2.8) can be combined to form a single second-order partial differential equation (PDE), which is a member of the class of nonlinear Klein-Gordon equations [18]. For this equation, it can be shown [18] that the derivative of the stationary bounce [Eq. (2.13) or (2.14)] is a solution of Eq. (2.22) with eigenvalue $\omega^2=0$, independent of $a$. This "translation" mode restores the translational invariance that was lost when the bounce was centered at $x=0$. We label the normalized eigenfunction as $\phi_1$, and it is

$$\phi_1(x) \propto \frac{du_b}{dx} = -\frac{\sqrt{3}a}{c_0}\frac{\frac{3}{\sqrt{2}}\sqrt{\frac{2}{9}-a}\sinh\left(\frac{2\sqrt{a}}{c_0}x\right)}{\left[1+\frac{3}{\sqrt{2}}\sqrt{\frac{2}{9}-a}\cosh\left(\frac{2\sqrt{a}}{c_0}x\right)\right]^{3/2}}. \tag{3.1}$$

Since $\phi_1(x)$ in Eq. (3.1) has odd parity, it cannot be the ground state of Eq. (2.22), and there is (at least) one other solution $\phi_0$ with a negative squared frequency, $\omega_0^2<0$. We then see from Eq. (2.25) that the bounce is actually a saddle point on the energy surface of the system and that the eigenfunction $\phi_0$ specifies a direction along which the evolution of the system is unstable.

By integrating Eq. (B2) for the case $K=2$, [cf. Eq. (2.2)] we obtain

$$\int_{-\infty}^{\infty} dx \frac{1}{2}c_0^2\left(\frac{du_b}{dx}\right)^2 = \int_{-\infty}^{\infty} dx V_1(u_b(x)), \tag{3.2}$$

which shows [cf. Eq. (2.1)] that the elastic and local potential energy contributions to the total energy are equal for the stationary bounce. Therefore,

$$E_b = c_0^2\int_{-\infty}^{\infty} dx\left(\frac{du_b}{dx}\right)^2, \tag{3.3}$$

and the normalized eigenfunction for the translation mode is

$$\phi_1(x) = \frac{c_0}{\sqrt{E_b}}\frac{du_b}{dx}. \tag{3.4}$$

### B. Manipulations on the eigenvalue equation

Several manipulations must be carried out on Eq. (2.22) in order to solve it. We describe those here but omit details. We substitute Eq. (2.13) into Eq. (2.22), we change the independent variable from $x$ to

$$y = \frac{\sqrt{a}}{c_0}x, \tag{3.5}$$

and we use identities for hyperbolic functions [$\cosh(2\theta)=2\cosh^2(\theta)-1$ and $\mathrm{sech}^2(\theta)=1-\tanh^2(\theta)$]. We introduce an important parameter

$$\nu(a) = \frac{1+\sqrt{1-\frac{9}{2}a}}{1-\sqrt{1-\frac{9}{2}a}}; \tag{3.6}$$

for $0<a<2/9$, $\infty>\nu>1$. We also change the eigenvalue by shifting it from $\omega^2$ to (the $1/4$ factor is for later convenience)

$$\lambda(a) = \frac{1}{4}\left(\frac{\omega^2}{a}-1\right). \tag{3.7}$$

Then Eq. (2.22) becomes

$$\frac{d^2\phi}{dy^2} + [4\lambda - v(y)]\phi = 0, \tag{3.8}$$

where the "potential energy" is

$$v(y) = \frac{-6(\nu+1)\mathrm{sech}^2 y}{\nu-\tanh^2 y} + \frac{15\nu\,\mathrm{sech}^4 y}{(\nu-\tanh^2 y)^2}. \tag{3.9}$$

It is also useful to substitute Eq. (2.14) into Eq. (2.22) and then carry out the same steps, which gives another form for $v(y)$:

$$v(y) = -\tfrac{15}{4}[\mathrm{sech}^2(y+y_0)+\mathrm{sech}^2(y-y_0)] + \frac{1}{\sqrt{2a}}[\tanh(y+y_0)-\tanh(y-y_0)] \tag{3.10}$$

[$y_0$ is obtained by substituting Eq. (2.15) into Eq. (3.5)]. Plots of $v(y)$ for several values of $a$ are shown in Fig. 3.

It is evident from Eqs. (3.9) and (3.10) and Fig. 3 that $v(y)$ is an even function of $y$ and that $v(y)\to 0$ for $y\to\pm\infty$. Therefore there is a finite number of discrete bound-state eigenvalues with $\lambda<0$ and a continuum for $\lambda>0$. In terms of the original eigenvalue $\omega^2$, there are discrete values for $\omega^2<a$ and a continuum for $\omega^2>a$. [We have already determined that there is one discrete level at $\omega^2=0$ and (at least) one more with $\omega^2<0$.] $v(y)$ has a single well for $0<a<32/225=0.14222\ldots$ and a double well for $32/225<a<2/9$. For $16/75=0.21333\ldots<a<2/9$, there is a symmetric interval around $y=0$ where $v(y)>0$ (see Fig. 3).

### C. Limiting cases

In the two end-point cases $a\to 0$ and $a\to 2/9$, Eqs. (3.8) and (3.9) reduce to well-known examples for the Schrödinger equation.

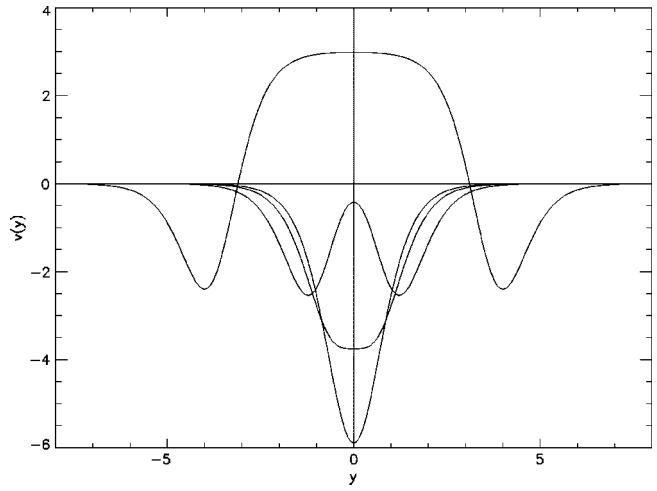


FIG. 3. From bottom to top along the ordinate, the "potential energy" function in Eq. (3.8) for $a=0.01$, 0.14223, 0.21, 0.222222.

#### 1. $a \to 0$

In this limit, from Eq. (3.6), $\nu(a) \to \infty$, and Eqs. (3.8) and (3.9) become

$$\frac{d^2\phi}{dy^2} + [(4\lambda) + 2(2+1)\mathrm{sech}^2\, y]\phi = 0. \tag{3.11}$$

The $n(n+1)\mathrm{sech}^2\, y$ potential well with integer $n$ is a standard example of a reflectionless potential in quantum mechanics [19,20]. There are two bound states with eigenvalues $4\lambda(a) = -4, -1$, which are equivalent to [cf. Eq. (3.7)] $\omega_0^2 \to -3a$ for $a \to 0$ and $\omega_1^2 = 0$. The lowest value corresponds to the unstable mode, and the second value to the translation mode, both of which we have previously identified.

#### 2. $a \to 2/9$

For $a \to 2/9$ the two minima in Eq. (3.9) separate to $\pm\infty$ (Fig. 3), so we change the independent variable to $z = y - y_0$ to place the right well at the origin and send the other to $-\infty$. The eigenvalues are doubly degenerate in this limit, since each state is duplicated at $\pm\infty$. Equations (3.8) and (3.9) become

$$\frac{d^2\phi}{dz^2} + \left\{(4\lambda) + \frac{15}{4}\mathrm{sech}^2\, z - \frac{3}{2}[1 - \tanh z]\right\}\phi = 0. \tag{3.12}$$

This equation is a special case of a textbook example [21], which has the result that Eq. (3.12) has a single bound state $\lambda(a=2/9) = -1$ or $\omega^2 = 0$. Because of the double degeneracy of this limit, there must be two $\omega^2$ eigenvalues that approach zero in this limit. One of these is the translation mode, with $\omega_1^2 = 0$ for every $a$ in the range $0 < a < 2/9$, and the other must be the unstable mode.

### D. Calculation of the spectrum

We continue the solution of Eqs. (3.8) and (3.9) by making another independent variable change similar to that used in Schrödinger equations with a $\mathrm{sech}^2(y)$ well—viz., to the variable $z = \tanh^2(y)$. The physical range of $y$ is $-\infty < y < \infty$, and this variable change gives a one-to-one map of half of that interval—say, $0 < y < \infty$—to the interval $0 < z < 1$. To obtain the solution on the other half of the range of $y$, we recall that the solutions have definite parity, and thus the solution on $-\infty < y < 0$ is obtained by symmetry. Equations (3.8) and (3.9) become

$$\frac{d^2\phi}{dz^2} + \left(\frac{1/2}{z} + \frac{1}{z-1}\right)\frac{d\phi}{dz} + \left[\frac{\lambda}{(z-1)^2} - \frac{15/4}{(z-\nu)^2} + \frac{(15/4 - \lambda)z + \nu(3/2 + \lambda) - 9/4}{z(z-1)(z-\nu)}\right]\phi = 0. \tag{3.13}$$

Inspection shows that this equation has three regular singular points [22] at $z=0$, 1, and $\nu(a)$, and it is straightforward to verify that there is a fourth regular singular point at $z=\infty$. The singular point at $\nu(a)$ [Eq. (3.6)] moves with changes in the value of the shape parameter $a$ or, equivalently, with changes in the separation of the soliton and antisoliton in the stationary bounce solution [Eq. (2.14)] or changes in the "potential energy" in the Schrödinger equation (Fig. 3). The characteristic exponents at each of these singularities, obtained from the Frobenius method of series solution [23], are given in Table I.

TABLE I. Characteristic exponents.

| $r$ | Regular singular points $z_r$ | Characteristic exponents |
|---|---|---|
| 1 | 0 | 0, 1/2 |
| 2 | 1 | $\pm\sqrt{-\lambda}$ |
| 3 | $\nu(a)$ | −3/2, 5/2 |
| 4 | $\infty$ | 0, 1/2 |

We now transform Eq. (3.13) so that one of the characteristic exponents at each of the finite singularities $z=0$, 1, and $\nu(a)$ is reduced to zero. The appropriate transformation is to a new dependent variable $A(z)$ defined by

$$\phi(z) = z^{-\xi}(z-1)^{-\mu}(z-\nu)^{-\kappa}A(z). \tag{3.14}$$

The exponents $\xi$, $\mu$, and $\kappa$ are the *negatives* of either one of the characteristic exponents at the respective singularity listed in Table I; i.e., each one is chosen to be one of the following possibilities:

$$\kappa = 3/2, -5/2;\ \xi = 0, -1/2;\ \mu = \pm\sqrt{-\lambda} \tag{3.15}$$

(recall that $\lambda < 0$ for bound states). The resulting equation is

$$\frac{d^2A}{dz^2} + \left(\frac{1/2 - 2\xi}{z} + \frac{1 - 2\mu}{z-1} - \frac{2\kappa}{z-\nu}\right)\frac{dA}{dz} + \left[\left(2\mu\kappa - \frac{3\kappa}{2} + 2\kappa\xi + 2\mu\xi - \frac{\mu}{2} - \xi + \frac{15}{4} - \lambda\right)z - 2\kappa\xi + \frac{\kappa}{2} - \frac{9}{4} + \nu\left(-2\mu\xi + \frac{\mu}{2} + \xi + \lambda + \frac{3}{2}\right)\right]\frac{A}{z(z-1)(z-\nu)} = 0. \tag{3.16}$$

TABLE II. Values of Heun parameters.

| $\kappa$ | $\xi$ | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ | $b_H$ |
|---|---|---|---|---|---|---|
| 3/2 | 0 | $-\mu-3/2$ | $-\mu-1$ | 1/2 | −3 | $-\nu(\mu+1)(\mu-3/2)-3/2$ |
| 3/2 | −1/2 | $-\mu-1$ | $-\mu-1/2$ | 3/2 | −3 | $-\nu(\mu+1/2)(\mu-2)$ |
| −5/2 | 0 | $-\mu+3$ | $-\mu+5/2$ | 1/2 | 5 | $-\nu(\mu+1)(\mu-3/2)-7/2$ |
| −5/2 | −1/2 | $-\mu+7/2$ | $-\mu+3$ | 3/2 | 5 | $-\nu(\mu+1/2)(\mu-2)-6$ |

Equation (3.16) is now in a canonical form known as the normal form of the Heun equation [8–10,24], which is

$$\frac{d^2A}{dz^2}+\left(\frac{\gamma}{z}+\frac{1+\alpha+\beta-\gamma-\delta}{z-1}+\frac{\delta}{z-\nu}\right)\frac{dA}{dz}+\frac{\alpha\beta z+b_H}{z(z-1)(z-\nu)}A=0. \tag{3.17}$$

Heun originally introduced this equation [8] with four regular singular points to generalize the hypergeometric equation, which has three regular singular points at 0, 1, and ∞. The constants $\alpha$, $\beta$, $\gamma$, and $\delta$ are related to the characteristic exponents of Eq. (3.17) at its singularities. However, an ordinary differential equation (ODE) with four regular singular points is not determined solely by the singularity structure [10], as it is for the hypergeometric equation; the Heun equation has an additional free parameter, which is the Heun accessory parameter $b_H$. We equate coefficients of corresponding terms in the generic Heun equation (3.17) and our Eq. (3.16) and solve for $\alpha$, $\beta$, $\gamma$, $\delta$, and $b_H$ in terms of our exponents $\xi$, $\kappa$, and $\mu$. The results are given in Table II, where the first two columns give the choices for $\kappa$ and $\xi$ from Eq. (3.15) and the remaining columns give $\alpha$, $\beta$, $\gamma$, $\delta$, and $b_H$. The entries for $\alpha$, $\beta$, and $b_H$ come out to be functions of the exponent $\mu$ and the parameter $\nu$. The eigenvalues λ require $\mu$ through Eq. (3.15), and the eigenfunctions require $\mu$ through Eq. (3.14). For a given value of the shape parameter $a$ [Eq. (2.2)] $\nu(a)$ is determined from Eq. (3.6), and thus the problem reduces to finding the allowed values of $\mu$ which give the physically appropriate solutions of Eq. (3.16).

Power series procedures have been developed to solve the Heun normal form, Eq. (3.17) and are described in Refs. [9,10,24]. We detail the application of these methods to our problem in Appendix D.

Figure 4 shows the results of the calculation in Appendix D. For an arbitrary value of $a$ in the range $0<a<2/9$ there are two discrete eigenvalues; one is the"ground" state with $\omega_0^2<0$, and the other is the first "excited" state, which is the translation mode with $\omega_1^2\equiv 0$. Then there is a continuous spectrum with $\omega^2>a$. The limiting values and degrees of degeneracy of $\omega^2$ at the ends of the $a$ range agree with the values obtained in Sec. III C. The negative value of $\omega_0^2$ shows that the bounce solution of the equation of motion is unstable and is a saddle point in the phase space of motions of the string. The corresponding eigenfunction $\phi_0(x)$ gives the unstable direction through this saddle point.

These results will be used in the next sections to calculate the nucleation rate.

## IV. STATISTICAL PROBLEM

To cause sections of the elastic string to flip over the barrier between the metastable and stable wells of the local potential energy, we add damping and noise forces, so that the EOM are modified from the deterministic Eqs. (2.7) and (2.8) to the Langevin or stochastic PDE's

$$u_t(x,t)=\pi(x,t),$$

$$\pi_t(x,t)=c_0^2u_{xx}-au+\tfrac{4}{3}u^3-\tfrac{3}{2}u^5-\gamma u_t(x,t)+\eta(x,t). \tag{4.1}$$

Here $\gamma$ is a damping constant and $\eta(x,t)$ is a random noise force density. The damping and noise forces result from coupling the system to a heat bath at temperature $T$. The probability distribution function (PDF) $\rho_\eta(\{\eta\})$ for the random force density $\eta(x,t)$ is assumed to be Gaussian:

$$\rho_\eta(\{\eta\})\propto\exp\left[-\frac{1}{4T\gamma}\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dt\,\eta^2(x,t)\right]. \tag{4.2}$$

With this PDF the mean value $\langle\eta(x,t)\rangle$ is zero and the correlation function is

$$\langle\eta(x,t)\,\eta(x',t')\rangle=2\gamma T\delta(x-x')\,\delta(t-t'). \tag{4.3}$$

Stochastic differential equations with a prescribed PDF for the noise terms are equivalent to a PDE, known as the Fokker-Planck equation (FPE), for the probability distribu-

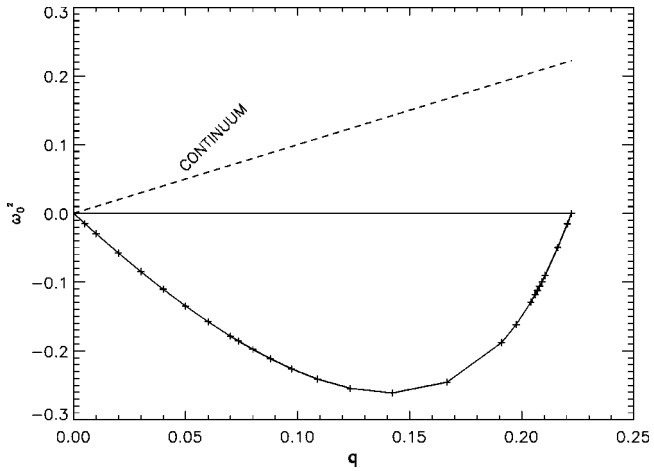


FIG. 4. The values of the squared frequencies for small oscillations for the two discrete eigenvalues for Eq. (2.22): the unstable mode with $\omega_0^2<0$ and the translation mode with $\omega_1^2=0$. The dashed line is the lower limit of the continuum, which begins at $\omega^2=a$.

tion function of the solutions [25–27]. For a continuum system, the set of solutions $\pi(x,t), u(x,t)$ of Eq. (4.1) for every specific realization of the random force $\eta(x,t)$ describes the phase space of possible motions of the system, and the PDF $\rho[\pi,u]$ is a functional of these functions. Because the system is a continuum, the FPE is a functional PDE on the full phase space of the system. It has the form of a continuity equation for the flow of probability in the phase space and is

$$\frac{\partial\rho}{\partial t} = -\int_{-\infty}^{\infty} dx \left\{ \frac{\delta J_{u,x}}{\delta u(x)} + \frac{\delta J_{\pi,x}}{\delta\pi(x)} \right\}. \tag{4.4}$$

The right-hand side of Eq. (4.4) is the phase-space divergence; one choice of coordinate axes in phase space is labeled by the canonical variables—that is, by both displacement and momentum at each $x$. For the noise PDF in Eq. (4.2), the components of the probability current along each axis in phase space are

$$J_{u,x}[\pi,u] = \frac{\delta H}{\delta\pi(x)}\rho + T\frac{\delta\rho}{\delta\pi(x)}, \tag{4.5}$$

$$J_{\pi,x}[\pi,u] = \left( -\frac{\delta H}{\delta u(x)} - \gamma\frac{\delta H}{\delta\pi(x)} \right)\rho - \gamma T\frac{\delta\rho}{\delta\pi(x)} - T\frac{\delta\rho}{\delta u(x)}. \tag{4.6}$$

Fokker-Planck equations for systems of discrete particles are given in many places in the literature [25–27], and our Eqs. (4.4)–(4.6) are obtained by placing these particles on a lattice and then taking the (one-dimensional) continuum limit. For example, from Eq. (2.1), $\delta H/\delta\pi(x) = \pi(x)$, and in our dimensionless units where the mass density is unity (cf. Appendix A), the momentum density is the same as the velocity. Therefore the first term in Eq. (4.5) is the familiar convective term $v\rho$. Similarly in Eq. (4.6), $-\delta H/\delta u(x)$ is the deterministic force density, and the terms proportional to $\gamma$ come from the coupling to the heat bath. The last terms in Eqs. (4.5) and (4.6) actually cancel between the two terms in Eq. (4.4), so they make no contribution to the FPE. We include them, following Ref. [15], so that the probability current vanishes for the equilibrium solution $\rho[\pi,u] \propto \exp(-H[\pi,u]/T)$ [28].

We reduce the time-dependent FPE (4.4) to a time-independent boundary value problem by using the procedure introduced by Farkas [29] (called the "flux-overpopulation method" [1]) and used by many of the subsequent papers on the subject—e.g., [13,15,30,31]. The method changes the initial value problem into a time-independent boundary value problem in which the distribution $\rho[\pi,u]$ approaches the thermal equilibrium solution in the metastable region of phase space, Eq. (2.10), and approaches zero in the stable region, Eq. (2.11). The procedure assumes that probability flowing into the lower well is immediately put back into the upper well to replenish it. This steady-state solution has current flowing over the "pass" at the saddle point, so that we can calculate the nucleation rate by integrating the current over a surface which passes through the saddle point. Thus the FPE we solve with the stated boundary conditions is

$$\int_{-\infty}^{\infty} dx \left\{ \frac{\delta J_{u,x}}{\delta u(x)} + \frac{\delta J_{\pi,x}}{\delta\pi(x)} \right\} = 0. \tag{4.7}$$

## V. SOLUTION FOR THE PHASE-SPACE PDF

Our method for solving Eq. (4.7) is obtained from solutions of the FPE already in the literature for other systems—e.g., [15,32]. We transform the dependent variable in the FPE according to

$$\rho[\pi,u] = B[\pi,u]\exp(-H[\pi,u]/T). \tag{5.1}$$

The boundary conditions on $\rho$, described at the end of Sec. IV, require $B$ to approach $1/Z_{ms}$ for the phase-space point $[\pi,u]$ approaching the metastable well [Eq. (2.10)] and to approach zero for $[\pi,u]$ approaching the stable well [Eq. (2.11)]. $Z_{ms}$ is the partition function for the metastable state; we will evaluate it later in the paper. In terms of $B$ the formulas for the current components are

$$J_{u,x}[\pi,u] = T\frac{\delta B}{\delta u(x)}\exp\left(-\frac{H}{T}\right),$$

$$J_{\pi,x}[\pi,u] = \left[ -\gamma T\frac{\delta B}{\delta\pi(x)} - T\frac{\delta B}{\delta u(x)} \right]\exp\left(-\frac{H}{T}\right). \tag{5.2}$$

Now we combine Eq. (5.2) with Eq. (C5) to obtain the components of the current along the eigenfunction directions:

$$J_{u,n}[\pi,u] = T\frac{\partial B}{\partial\xi_n}\exp\left(-\frac{H}{T}\right),$$

$$J_{\pi,n}[\pi,u] = \left( -\gamma T\frac{\partial B}{\partial\xi_n} - T\frac{\partial B}{\partial\zeta_n} \right)\exp\left(-\frac{H}{T}\right). \tag{5.3}$$

The next step is to use Eq. (C8) to rewrite the equation to be solved, the vanishing of the divergence of the phase-space current Eq. (4.7), in terms of the eigenfunction directions. To compute the derivatives of the current, we recognize that we need to know the current only in the vicinity of the saddle point, so it is sufficient to use Eq. (2.25) for the Hamiltonian. The derivatives are

$$\frac{\partial J_{u,n}}{\partial\zeta_n} = \left[ T\frac{\partial^2 B}{\partial\zeta_n\partial\xi_n} - \omega_n^2\zeta_n\frac{\partial B}{\partial\xi_n} \right]\exp\left(-\frac{H}{T}\right), \tag{5.4}$$

$$\frac{\partial J_{\pi,n}}{\partial\xi_n} = \left[ \left( -\gamma T\frac{\partial^2 B}{\partial\xi_n^2} - T\frac{\partial^2 B}{\partial\xi_n\partial\zeta_n} \right) + \left( \gamma\frac{\partial B}{\partial\xi_n} + \frac{\partial B}{\partial\zeta_n} \right)\xi_n \right] \times\exp\left(-\frac{H}{T}\right). \tag{5.5}$$

The requirement that the divergence of $J$ vanish [Eqs. (4.7) and (C8)] now gives the equation for $B$, which is (after some cancellations)

$$\sum_n \left[ -\gamma T\frac{\partial^2 B}{\partial\xi_n^2} + (\gamma\xi_n - \omega_n^2\zeta_n)\frac{\partial B}{\partial\xi_n} + \xi_n\frac{\partial B}{\partial\zeta_n} \right] = 0. \tag{5.6}$$

To solve the infinite-dimensional PDE (5.6), we employ the technique initiated by Kramers [13] to reduce it to an

ODE. We assume that $B$ is a function of only a single variable $y$ which is related to the $\zeta_n$'s and $\xi_n$'s by

$$y = \sum_n (R_n \zeta_n + S_n \xi_n), \tag{5.7}$$

with parameters $R_n$, $S_n$ to be determined. With this assumption Eq. (5.6) becomes

$$\left( - \sum_n \gamma T S_n^2 \right) \frac{d^2 B}{dy^2} + \left\{ \sum_n [(\gamma S_n + R_n)\xi_n - \omega_n^2 S_n \zeta_n] \right\} \frac{dB}{dy} = 0. \tag{5.8}$$

In order for this to be an ODE, the coefficient of $dB/dy$ must be proportional to $y$:

$$\sum_n [(\gamma S_n + R_n)\xi_n - \omega_n^2 S_n \zeta_n] = (-A) y = (-A) \sum_n (R_n \zeta_n + S_n \xi_n). \tag{5.9}$$

Linear independence of the $\xi_n$'s and $\zeta_n$'s requires

$$(\gamma + A) S_n + R_n = 0,$$

$$- \omega_n^2 S_n + A R_n = 0; \tag{5.10}$$

these must hold for all $n$. To have a nontrivial solution for $R_n$ and $S_n$, the proportionality coefficient $A$ must be

$$A = \frac{\gamma}{2} \left[ \pm \sqrt{1 - \left( \frac{4\omega_n^2}{\gamma^2} \right)} - 1 \right]. \tag{5.11}$$

Equations (5.10) must hold for all $n$, but Eq. (5.11) can apply for only one $n$ value, since there can be only one $A$ value. The only way to satisfy these conditions is for $R_n = S_n = 0$ for all but one $n$ value, call it $n^*$, and then $A$ is determined by $\omega_{n^*}^2$. Next we must determine $n^*$.

With Eq. (5.9) satisfied, Eq. (5.8) becomes

$$\frac{d^2 B}{dy^2} + \frac{A}{\gamma T S_{n^*}^2} y \frac{dB}{dy} = 0. \tag{5.12}$$

The solution of Eq. (5.12) is

$$\frac{dB}{dy} \propto \exp\left( - \frac{A y^2}{2 \gamma T S_{n^*}^2} \right), \; B(y) \propto \int^y dy' \exp\left( - \frac{A y'^2}{2 \gamma T S_{n^*}^2} \right). \tag{5.13}$$

The only way for $B(y)$ to give a normalizable distribution is to have $A > 0$. To see how that can be achieved, we return to Eq. (5.11). The only way to have $A > 0$ is to use the plus sign on the first term *and* to have $\omega_{n^*}^2 < 0$. Now we recall that because the bounce is a saddle point on the energy surface and therefore has an unstable direction passing through it, there *is* a negative squared frequency, and it is for $n^* = 0$. The correct value of $A$ is

$$A = \frac{\gamma}{2} \left[ \sqrt{1 + \left( \frac{4|\omega_0^2|}{\gamma^2} \right)} - 1 \right], \tag{5.14}$$

which is obviously positive. With this choice of $n^*$ we have achieved a suitable solution for the phase-space PDF.

We have shown that only the $n = 0$ terms are allowed in Eqs. (5.7)–(5.9). Equations (5.10) determine the ratio $S_0/R_0$, which is

$$\frac{S_0}{R_0} = - \frac{\gamma}{2|\omega_0^2|} \left[ \sqrt{1 + \frac{4|\omega_0^2|}{\gamma^2}} - 1 \right] \tag{5.15}$$

and which shows that $S_0$ and $R_0$ have opposite signs. We choose to have the variable $y$, which now is $y = R_0 \zeta_0 + S_0 \xi_0$ from Eq. (5.7), become negative when the phase-space point $[\pi, u]$ moves from the saddle point (the bounce solution) toward the metastable region and positive when it moves toward the stable region. We also choose the phase of the nodeless eigenfunction $\phi_0$ so that it is positive. Therefore we must choose $R_0 > 0$, and consequently $S_0 < 0$. The solution for $B$ that satisfies the boundary conditions specified earlier is

$$B(y) = \frac{1}{Z_{ms}} \sqrt{\frac{A}{2\pi\gamma T S_0^2}} \int_y^\infty dy' \exp\left( - \frac{A y'^2}{2 \gamma T S_0^2} \right). \tag{5.16}$$

This form for the solution assumes that the saddle point is sharp and well isolated from both the metastable and stable minima. Then the metastable minimum is described by $y \to -\infty$ and the stable minimum by $y \to \infty$. We change the integration variable in Eq. (5.16) to $y'' = y'/|S_0|$ so that

$$B(y) = \frac{1}{Z_{ms}} \sqrt{\frac{A}{2\pi\gamma T}} \int_{y/|S_0|}^\infty dy'' \exp\left( - \frac{A y''^2}{2 \gamma T} \right). \tag{5.17}$$

The final result for the phase-space PDF is obtained by combining Eq. (5.17) with Eq. (5.1) to obtain

$$\rho[\pi, u] = \frac{\exp(-H/T)}{Z_{ms}} \sqrt{\frac{A}{2\pi\gamma T}} \int_{(R_0/|S_0|)\zeta_0 - \xi_0}^\infty dy'' \exp\left( - \frac{A y''^2}{2 \gamma T} \right). \tag{5.18}$$

This way of writing the solution shows that it depends only on the ratio $R_0/S_0$ and not on the separate factors. $\zeta_0$ and $\xi_0$ are the components of the displacement and momentum density fluctuations about the bounce in the direction of the unstable eigenvector, from Eqs. (2.23) and (2.24). This solution of the FPE correctly approaches both the (normalized) thermal equilibrium distribution in the metastable state and zero in the stable state.

## VI. CALCULATION OF THE NUCLEATION RATE

To obtain the nucleation rate, we need expressions for the probability current near the saddle point, which we obtain from Eqs. (5.3) using our solution for $B$. The derivatives of $B$ that appear in Eqs. (5.3) are evaluated using Eq. (5.7)—e.g., $\partial B/\partial \xi_m = (dB/dy)(\partial y/\partial \xi_m)$. We showed in Sec. V that $y$ depends only on $R_0$ and $S_0$. Therefore, near the saddle point in phase space only the components of the current in the unstable direction are nonzero:

$$J_{u,0} = T S_0 \frac{dB}{dy} \exp\left( - \frac{H}{T} \right), \tag{6.1}$$

$$J_{\pi,0} = -T(\gamma S_0 + R_0)\frac{dB}{dy}\exp\left(-\frac{H}{T}\right). \tag{6.2}$$

We note that

$$J_{\pi,0} = -\left(\gamma + \frac{R_0}{S_0}\right)J_{u,0}. \tag{6.3}$$

From Eq. (5.17),

$$\frac{dB}{dy} = -\frac{1}{Z_{ms}}\sqrt{\frac{A}{2\pi\gamma T}}\exp\left[-\frac{A}{2\gamma T}\left(\frac{y}{|S_0|}\right)^2\right]\frac{1}{|S_0|}. \tag{6.4}$$

The zeroth component of the displacement part of the probability current is (noting that $S_0/|S_0| = -1$)

$$J_{u,0}[\pi,u] = T\frac{1}{Z_{ms}}\sqrt{\frac{A}{2\pi\gamma T}} \times\exp\left[-\frac{A}{2\gamma T}\left(\frac{R_0}{|S_0|}\zeta_0 - \xi_0\right)^2\right]\exp\left(-\frac{H}{T}\right). \tag{6.5}$$

These equations hold only near the saddle point, so we use Eq. (2.25) for the Hamiltonian and obtain

$$J_{u,0}[\pi,u] = T\frac{1}{Z_{ms}}\sqrt{\frac{A}{2\pi\gamma T}}e^{-E_b/T}\exp\left[-\frac{1}{2T}\sum_n(\xi_n^2 + \omega_n^2\zeta_n^2) - \frac{A}{2\gamma T}\left(\frac{R_0}{|S_0|}\zeta_0 - \xi_0\right)^2\right]. \tag{6.6}$$

We obtain the other nonzero component of the probability current from Eq. (6.3).

To obtain the nucleation rate we integrate the probability current over any surface passing through the saddle point whose normal is not perpendicular to the current. It is easiest to pick the surface whose normal is in the $\zeta_0$ direction, so we only need the $J_{u,0}$ component; the $J_{\pi,0}$ component is orthogonal to this direction. Also, since the surface passes through the saddle point, we set $\zeta_0 = 0$. The nucleation rate is the integral over all the other variables:

$$I = T\frac{1}{Z_{ms}}\sqrt{\frac{A}{2\pi\gamma T}}e^{-E_b/T}\int_{-\infty}^{\infty}d\xi_0\exp\left(-\frac{\xi_0^2}{2T} - \frac{A}{2\gamma T}\xi_0^2\right) \times\left[\prod_{n\geqslant 1}\int_{-\infty}^{\infty}d\xi_n e^{-\xi_n^2/2T}\right]\int_{-\infty}^{\infty}d\zeta_1\left[\prod_{n\geqslant 2}\int_{-\infty}^{\infty}d\zeta_n e^{-\omega_n^2\zeta_n^2/2T}\right]. \tag{6.7}$$

The Gaussian integrals here are elementary, but we give the evaluation of the one over $\xi_0$:

$$\sqrt{\frac{A}{2\pi\gamma T}}\int_{-\infty}^{\infty}d\xi_0\exp\left(-\frac{\xi_0^2}{2T} - \frac{A}{2\gamma T}\xi_0^2\right) = \frac{\gamma}{2\sqrt{|\omega_0^2|}}\left[\sqrt{1 + \frac{4|\omega_0^2|}{\gamma^2}} - 1\right]. \tag{6.8}$$

The integral over the coefficient of the translation mode, $d\zeta_1$, requires separate evaluation [16]. Any fluctuation about the bounce solution $u_b(x)$ can be expanded as shown in Eq. (2.23). We consider a very particular fluctuation—namely, the one produced by shifting the bounce solution an infinitesimal amount $dx$:

$$u_b(x + dx) - u_b(x) = \frac{du_b}{dx}dx = \sum_n d\zeta_n\phi_n(x). \tag{6.9}$$

In Eq. (3.1) we showed that the derivative of the bounce $du_b/dx$ is proportional to the eigenfunction $\phi_1$, so only the $n = 1$ term is nonzero in Eq. (6.9). Equation (3.4) gives the proportionality factor between $du_b/dx$ and $\phi_1$. Combining these two equations gives $d\zeta_1 = (\sqrt{E_b}/c_0)dx$, and then the integral needed in Eq. (6.7) is

$$\int_{-\infty}^{\infty}d\zeta_1 = \frac{\sqrt{E_b}}{c_0}L, \tag{6.10}$$

where $L$ is the system length. The nucleation rate is extensive in the thermodynamic limit $L\to\infty$. (If we had considered a finite system with specific boundary conditions, the dependence on the system size would be different [33].) To this point we have the following result for the nucleation rate per unit length:

$$\frac{I}{L} = Te^{-E_b/T}\frac{\sqrt{E_b}}{c_0}\frac{\gamma}{2\sqrt{|\omega_0^2|}}\left[\sqrt{1 + \frac{4|\omega_0^2|}{\gamma^2}} - 1\right] \times\frac{1}{Z_{ms}}\prod_{n\geqslant 1}\int_{-\infty}^{\infty}d\xi_n e^{-\xi_n^2/2T}\prod_{n\geqslant 2}\int_{-\infty}^{\infty}d\zeta_n e^{-\omega_n^2\zeta_n^2/2T}, \tag{6.11}$$

where $Z_{ms}$ is the partition function obtained from the Hamiltonian expanded around the metastable minimum, Eq. (2.27). The factor in $Z_{ms}$ coming from the kinetic energy cancels the integrals over $\xi_n$ in Eq. (6.11), except that the numerator has one fewer factor than the denominator because of the $n\geqslant 1$ restriction. Then, the integrals over $\zeta_n$ in Eq. (6.11) and coming from $\zeta_{n,ms}$ in Eq. (2.27) have the same form but with different frequencies. The restriction $n\geqslant 2$ in the numerator means that there are two fewer factors in the numerator than in the denominator. The ratio of these integrals is

$$\prod_{n\geqslant 2}\sqrt{\frac{2\pi T}{\omega_n^2}}\left[\prod_n\sqrt{\frac{2\pi T}{\omega_{ms,n}^2}}\right]^{-1} = \frac{1}{2\pi T}\frac{\prod_n\omega_{ms,n}}{\prod_{n\geqslant 2}\omega_n}. \tag{6.12}$$

The nucleation rate per length is now

$$\frac{I}{L} = \frac{1}{(2\pi)^{3/2}}\frac{1}{c_0}e^{-E_b/T}\sqrt{\frac{E_b}{T}}\frac{\gamma}{2\sqrt{|\omega_0^2|}}\left[\sqrt{1 + \frac{4|\omega_0^2|}{\gamma^2}} - 1\right]Q, \tag{6.13}$$

where

$$Q = \frac{\prod_n \omega_{ms,n}}{\prod_{n\geqslant 2} \omega_n} = a \frac{\prod_n \sqrt{\omega_{ms,n}^2/a}}{\prod_{n\geqslant 2} \sqrt{\omega_n^2/a}}. \tag{6.14}$$

The ratios $\omega_n^2/a$ are introduced because they are related to the eigenvalues of the Schrödinger equation in Eq. (3.8). The prefactor of $a$ results because the numerator has two fewer factors than the denominator.

Our final problem is to evaluate $Q$ in Eq. (6.14), which involves only continuum modes for both metastable and bounce solutions. We square $Q$, take its logarithm, write the resulting sums in terms of the density of states function (DOS) for squares of the frequencies of the metastable modes and continuum part of the bounce modes, and then take the square root. That is,

$$Q = a \exp\left\{ \frac{1}{2} \int_1^\infty d\tilde{\epsilon} [\tilde{\rho}_{ms}(\tilde{\epsilon}) - \tilde{\rho}_b(\tilde{\epsilon})] \ln \tilde{\epsilon} \right\}. \tag{6.15}$$

The DOS for the bounce modes is defined by

$$\tilde{\rho}_b(\tilde{\epsilon}) = \sum_{n\geqslant 2} \delta(\tilde{\epsilon} - \omega_n^2/a); \tag{6.16}$$

the DOS for the continuum modes has a similar definition in terms of the corresponding squared frequencies $\omega_{ms,n}^2/a$ and the sum on $n$ is over all continuum modes. The lower limit of the integral in Eq. (6.15) expresses the fact that the lower limit on the continuum for both sets of modes is at $\omega^2 = a$. The final step is to shift the integration variable in Eq. (6.15) to $\epsilon = \tilde{\epsilon} - 1$—i.e., $\epsilon = \omega^2/a - 1$ [34]. We define shifted DOS functions for both sets of modes by $\rho(\epsilon) = \tilde{\rho}(1+\epsilon)$ and obtain

$$Q = a \exp\left\{ \frac{1}{2} \int_0^\infty d\epsilon [\rho_{ms}(\epsilon) - \rho_b(\epsilon)] \ln(1+\epsilon) \right\}. \tag{6.17}$$

For the metastable modes the DOS is obtained from a Klein-Gordon equation and is well known. To obtain the DOS for the bounce modes, we use a WKB approximation, similarly to the procedure used by Büttiker and Landauer [32]. The details are given in Appendix E.

Equations (6.13), (6.17), and (E11) are our final formal result for the nucleation rate per unit length. Equation (2.16) gives the bounce energy $E_b$ as a function of shape parameter $a$ and characteristic velocity $c_0$; it is proportional to $c_0$. From the way that $c_0$ enters in Eq. (6.13), we see that if $c_0 I/L$ is plotted as a function of $c_0/T$, then, for given values of the shape parameter $a$ and the damping constant $\gamma$, a single curve is obtained.

Numerical results for the nucleation rate are obtained by using the values for the discrete eigenvalue $\omega_0^2$ and the results for $Q$ from the calculations in Appendix E. These are given in the next section.

## VII. NUMERICAL RESULTS

In Figs. 5 and 6 we show the logarithm of the nucleation rate per unit length as a function of inverse temperature for a fixed value of the damping constant and for a range of values for the shape parameter $a$. The ordinate and abscissa have been scaled by $c_0$ as discussed in the preceding section. The value of $\gamma$ satisfies $\gamma > \sqrt{|\omega_0^2(a)|}$ for all $a$. This condition is sufficient for the calculations to be in the range where the theory in the preceding sections is valid [1]. However, it is not a necessary condition [35].

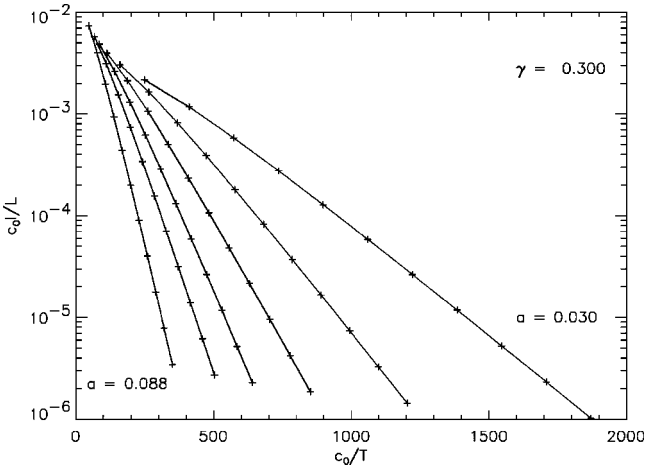


FIG. 5. Temperature dependence of the scaled nucleation rate for $\gamma = 0.3$ and for different $a$ values. From right to left, $a = 0.030$, 0.040, 0.050, 0.060, 0.070, 0.0878.

Unfortunately, at the present time there do not appear to be any existing experiments or simulations to which these results could be compared.

The results presented here should be contrasted with our earlier results for the asymmetric $\phi^4$ local potential energy [7]. The range of temperature was much smaller in [7], due to the limited temperature range of the simulation results available for comparison there. The temperature range shown here is large enough to show the deviation from linearity on a semilogarithmic plot caused by the temperature dependence of the prefactor in Eq. (6.13). For a given $a$ this deviation is most pronounced at large $T$. It is also larger for the smaller $a$ values.

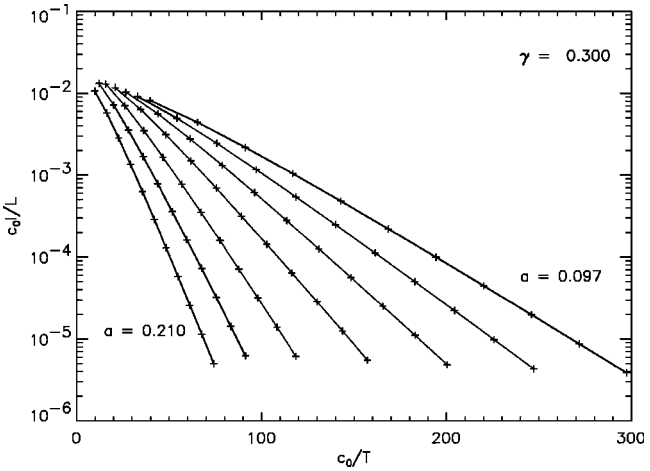


FIG. 6. Temperature dependence of the scaled nucleation rate for $\gamma = 0.3$ and for different $a$ values. From right to left, $a = 0.0972$, 0.109, 0.124, 0.142, 0.167, 0.191, 0.210.

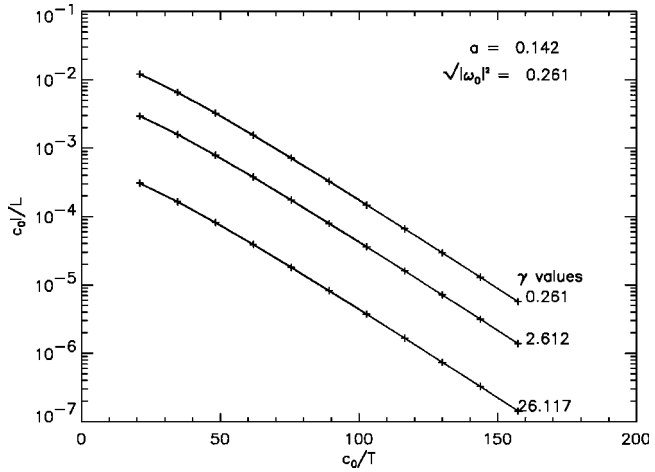


FIG. 7. Scaled nucleation rate per unit length, $c_0 I/L$ as a function of $c_0/T$ for fixed $a$ and for different $\gamma$ values.

Figure 7 shows the nucleation rate per unit length as a function of inverse $T$ for an intermediate value of $a$ for three different values of the damping constant $\gamma$. Not surprisingly, the rate decreases rather uniformly for increasing $\gamma$.

The temperature dependence of the preexponential factor found here in Eq. (6.13) and in [7] is proportional to $T^{-1/2}$. This result agrees with [5], where it is claimed that this is the universal temperature dependence (outside the quantum tunneling regime). That claim was made on the basis of a theory valid only where the local potential energy was only slightly asymmetric (i.e., the $a \to 2/9$ limit for our system). We have found that dependence here for all values of the shape parameter.

## VIII. SUMMARY

In summary we have presented a calculation of the nucleation rate of critical droplets on a continuum one-dimensional elastic string moving in a symmetric $\phi^6$ local potential energy. We have shown that the evaluation of the spectrum of small oscillations about the critical droplet can be done by solving a Heun equation. For this system this spectrum has two discrete states: the unstable mode and the translation mode. We have presented the details of the solution of the functional Fokker-Planck equation on the phase space of this continuum system, which involves projecting the equation onto the eigenfunction directions obtained from the Heun equation. These results are exact except for the use of the WKB approximation to obtain the frequency ratios of the continuum small oscillation modes about the critical droplet and the metastable minimum.

A subject for future work would be to extend the use of the Heun equation to discuss the case of weak damping, where different methods are required [13]. A further problem is to obtain a generalization that treats the whole range of damping; this is the so-called "Kramers turnover problem," which so far seems to have been treated only for the single-particle problem [35–42] and not for a continuum system.

## APPENDIX A: SCALE FACTORS

In this appendix we begin with the more general Hamiltonian with a parameter $K$ [7]:

$$H = \int_{-\infty}^{\infty} dx \left\{ \frac{\pi^2}{2\rho_M} + \frac{1}{2} c_0^2 \left( \frac{\partial u}{\partial x} \right)^2 + \rho_M \left[ \frac{1}{2} A u^2 - \frac{B}{K+2} u^{K+2} + \frac{C}{2K+2} u^{2K+2} \right] \right\}, \tag{A1}$$

where $\rho_M$ is mass density and all factors have dimensions. The case $K=1$ is the asymmetric $\phi^4$ system and $K=2$ gives the $\phi^6$ system considered in the main text. The local potential energy $V_1(u)$ [quantity in square brackets in Eq. (A1)] has dimensions of $(L/T)^2$ (i.e., velocity squared). Therefore we introduce a velocity unit

$$v_0 = \sqrt{\left( \frac{K+1}{2} \right)^{1+2/K} \left( \frac{3}{K+2} \right)^{2+2/K} \frac{B^{2+2/K}}{C^{1+2/K}}},$$

a length unit

$$l_0 = \left[ \frac{3}{2} \left( \frac{K+1}{K+2} \right) \frac{B}{C} \right]^{1/K},$$

and the time unit obtained from these:

$$t_0 = \frac{l_0}{v_0} = \left( \frac{2}{K+1} \right)^{1/2} \left( \frac{K+2}{3} \right) \frac{\sqrt{C}}{B}.$$

With these scale factors, the nondimensional form of the local potential energy is

$$V_1(u) = \tfrac{1}{2} a u^2 - \tfrac{1}{3} u^{K+2} + \tfrac{1}{4} u^{2K+2}, \tag{A2}$$

where the shape parameter is

$$a = \frac{2}{9} \frac{(K+2)^2}{K+1} \frac{AC}{B^2}. \tag{A3}$$

We choose $\rho_M$ to be the unit of mass density; then $\rho_M$, $l_0$, and $t_0$ can be combined to form the unit of any other physical quantity. The text considers the $K=2$ case of these equations.

## APPENDIX B: SOLUTION OF Eq. (2.9)

We start by considering the more general version of Eq. (2.9) obtained by using the local potential energy from Eq. (A2):

$$u''(x) = \frac{1}{c_0^2} \frac{d}{du} \left( \frac{1}{2} a u^2 - \frac{1}{3} u^{K+2} + \frac{1}{4} u^{2K+2} \right). \tag{B1}$$

It has been noted by several authors [16,43,44] that by considering $x$ to be "time," this equation is analogous to Newton's second law for a particle moving in one dimension in the *inverted* potential energy $[-V_1(u)]$. This observation allows integration of Eq. (B1) by elementary techniques. From the shape of the inverted potential energy (see Fig. 1 for the $K=2$ case), we see that there is a solution with zero "energy" in which the particle starts at $u=0$ at "time" $x=-\infty$, moves across the well in the inverted potential energy until it reaches the first zero of $[-V_1(u)]$ at positive $u$, and then decreases back to $u=0$ at "time" $x=+\infty$. This is the "bounce" solution that satisfies the boundary conditions described in Sec. II, and we refer to it as $u_b(x)$. The first integral of Eq.

(B1) with integration constant chosen to be consistent with this description is

$$[u_b'(x)]^2 = \frac{2}{c_0^2}\left(\frac{1}{2}au_b^2 - \frac{1}{3}u_b^{K+2} + \frac{1}{4}u_b^{2K+2}\right). \tag{B2}$$

We change the dependent variable here to

$$g(x) = [u(x)]^K \tag{B3}$$

and find that $g$ satisfies the equation

$$(g')^2 = \frac{2K^2}{c_0^2}\left(\frac{1}{2}ag^2 - \frac{1}{3}g^3 + \frac{1}{4}g^4\right). \tag{B4}$$

Except for the $K^2$ factor, Eq. (B4) is the "quasienergy" conservation equation for the bounce solution of the $K=1$ case of Eq. (A2), which is the potential energy function of an asymmetric $\phi^4$ system. That is, all values of $K>0$ in the local potential energy, Eq. (A2), can be reduced to solving the $K=1$ case with an extra factor of $K^2$. The solution of Eq. (B4) is given in several places in the literature—for example, [45–47]—and is

$$g(x) = \frac{3a}{1 + \frac{3}{2}\sqrt{2\left(\frac{2}{9} - a\right)}\cosh\left[\frac{K\sqrt{a}}{c_0}(x - x_{max})\right]}. \tag{B5}$$

$x_{max}$ is the location of the center and maximum of the bounce, and it enters the solution as an integration constant. The arbitrariness of the location of the bounce center expresses the translational invariance of the system and leads to the translation mode discussed in Sec. III A. For $K=2$ the transformation back to the original function $u(x)$ [Eq. (B3)] gives the result for the bounce given in Eq. (2.13). The other form given in Eq. (2.14) is obtained using identities for hyperbolic functions. For the $K=2$ case another solution is obtained by taking the negative square root. It describes the symmetrical situation where the critical droplet forms toward the left minimum of $V_1(u)$.

## APPENDIX C: CHANGE OF VARIABLE IN FUNCTIONAL DERIVATIVES

We consider a scalar functional $B$ of two one-dimensional fields $(\pi(x), u(x))$. (The notation is the same as in the main body of the paper, but the functional and the fields are not necessarily the same physical quantities as considered there.) When the fields are changed from arbitrary but definite choices $(\pi, u)$ to some infinitesimally close fields $(\pi + \delta\pi,\ u + \delta u)$, the functional changes by

$$dB = B[\pi + \delta\pi, u + \delta u] - B[\pi, u], \tag{C1}$$

and by definition of functional derivative this is the same as

$$dB = \int dx\left[\frac{\delta B}{\delta\pi(x)}\delta\pi(x) + \frac{\delta B}{\delta u(x)}\delta u(x)\right]. \tag{C2}$$

In terms of some complete orthonormal set of *real* functions $\{\phi_n\}$, the changes in the fields have expansions

$$\delta\pi(x) = \sum_n \delta\xi_n\phi_n(x),$$

$$\delta u(x) = \sum_n \delta\zeta_n\phi_n(x). \tag{C3}$$

We substitute Eqs. (C3) into Eq. (C2) and obtain

$$dB = \sum_n\left[d\xi_n\int dx\frac{\delta B}{\delta\pi(x)}\phi_n(x) + d\zeta_n\int dx\frac{\delta B}{\delta u(x)}\phi_n(x)\right]. \tag{C4}$$

Since the fields in the functional $B$ are completely specified by their expansion coefficients with respect to the set $\{\phi_n\}$, $B$ can equivalently be thought of as a function of this infinite set of coefficients—i.e., $B[\pi, u] \equiv B(\xi_0, \xi_1, \ldots; \zeta_0, \zeta_1, \ldots)$. We compare Eq. (C4) to the familiar equation from multivariable calculus for the differential in terms of partial derivatives and obtain

$$\frac{\partial B}{\partial\xi_n} = \int dx\frac{\delta B}{\delta\pi(x)}\phi_n(x),\ \frac{\partial B}{\partial\zeta_n} = \int dx\frac{\delta B}{\delta u(x)}\phi_n(x). \tag{C5}$$

The functional derivatives are evaluated at the initial point in phase space $[\pi, u]$.

Now suppose we have a phase-space vector functional of these fields—e.g., $(J_{u,x}[\pi, u], J_{\pi,x}[\pi, u])$. Since the complete orthonormal set of real functions $\{\phi_n(x)\}$ is the unitary transformation between the $x$ representation and the $n$ representation, the components along the directions of this orthonormal set are

$$J_{u,n}[\pi, u] = \int dy J_{u,y}[\pi, u]\phi_n(y),$$

$$J_{\pi,n}[\pi, u] = \int dy J_{\pi,y}[\pi, u]\phi_n(y). \tag{C6}$$

Using Eq. (C5), we obtain, from Eq. (C6),

$$\frac{\partial J_{u,n}}{\partial\zeta_m} = \int dx\frac{\delta J_{u,n}}{\delta u(x)}\phi_m(x) = \int dx\frac{\delta}{\delta u(x)}\int dy J_{u,y}\phi_n(y)\phi_m(x), \tag{C7}$$

and similarly for $\partial J_{\pi,n}/\partial\xi_m$. Next we add these two derivatives, set $m=n$, and sum on $n$. In the resulting expression the completeness relation $\Sigma_n\phi_n(y)\phi_n(x) = \delta(y-x)$ appears, and we obtain another way to write the phase-space divergence:

$$\sum_n\left[\frac{\partial J_{u,n}}{\partial\zeta_n} + \frac{\partial J_{\pi,n}}{\partial\xi_n}\right] = \int dx\left[\frac{\delta J_{u,x}}{\delta u(x)} + \frac{\delta J_{\pi,x}}{\delta\pi(x)}\right]. \tag{C8}$$

## APPENDIX D: SOLUTION OF Eq. (3.16)

Procedures that have been developed to solve the Heun normal form, Eq. (3.17), are described in Refs. [9,10,24], and

we have adapted those to our problem, in which the parameters in Eq. (3.17) are constrained by the conditions in Table II. The fundamental solution of Eq. (3.17) is the power series about $z=0$ associated with the characteristic exponent zero. A power series $\Sigma_{j=0}^{\infty} c_j z^j$ substituted into Eq. (3.17) comes out to be [9]

$$A(z) \equiv A(\nu, b_H; \alpha, \beta, \gamma, \delta; z) = 1 - \frac{b_H}{\gamma\nu} z + \sum_{j=2}^{\infty} c_j z^j. \quad \text{(D1)}$$

The coefficients $c_j$ for $j \geqslant 2$ are determined from a three term recursion relation

$$\nu(j+1)(j+\gamma)c_{j+1} - \{j^2(\nu+1) + j[\gamma+\delta-1+(\alpha+\beta-\delta)\nu] - b_H\}c_j + (j-1+\alpha)(j-1+\beta)c_{j-1} = 0,\ j \geqslant 1, \quad \text{(D2)}$$

starting from $c_0=1$ and $c_1=-b_H/(\gamma\nu)$. We divide this equation by $j^2 c_j$ ($j \geqslant 1$), both to obtain an equation for the coefficient ratio $R_j=c_{j+1}/c_j$ and to obtain coefficients that have a limit as $j \to \infty$:

$$\nu\left(1+\frac{1}{j}\right)\left(1+\frac{\gamma}{j}\right)R_j - \left\{\nu+1+\frac{1}{j}[\gamma+\delta-1+(\alpha+\beta-\delta)\nu] - \frac{b_H}{j^2}\right\} + \left(1+\frac{\alpha-1}{j}\right)\left(1+\frac{\beta-1}{j}\right)\frac{1}{R_{j-1}} = 0,\ j \geqslant 1. \quad \text{(D3)}$$

By knowing the limit of the ratio of the coefficients, we can use the ratio test to determine whether our series converges and to determine its radius of convergence. We introduce $R_\infty = \lim_{j\to\infty} R_j$, and then from Eq. (D3) we have that $R_\infty$ must be a solution of

$$\nu R_\infty^2 - (\nu+1)R_\infty + 1 = 0. \quad \text{(D4)}$$

This equation has the pair of roots $R_{\infty,1}=1/\nu$ and $R_{\infty,2}=1$. Equation (3.6) shows that $0<1/\nu<1$, so these two roots are unequal except at the extreme value $\nu=1$, which is the $a=2/9$ limit for the shape parameter [Eq. (2.2)], where we already know the answer [Sec. III C]. We now quote from Refs. [10,24] the conclusion of a theory due to Perron. If the roots of Eq. (D4) have different moduli with $|R_{\infty,1}|<|R_{\infty,2}|$, then in general $\lim_{j\to\infty}|R_j|$ exists and takes the larger value $|R_{\infty,2}|$. In our case $R_{\infty,2}=1$, so the ratio test shows that our series converges only in a restricted interval around $z=0$ that does not include $z=1$. Perron's theory further states that if the Heun accessory parameter $b_H$ takes on certain special values, then $\lim_{j\to\infty}|R_j|$ equals the smaller root $R_{\infty,1}$. Since $R_{\infty,1}=1/\nu<1$, convergence of the series is assured, with a radius of convergence that is larger than 1, and therefore our series converges at two singular points $z=0$ and $z=1$. It was in order to make this use of Perron's theorem that we chose the parametrization in our Heun equation so that the "moving" singularity would have the property $\nu(a)>1$. In our application we need convergence at both $z=0$ and $z=1$. These points are $y=0$ and $y=\infty$ of the position variable in our Schrödinger equation, and we need the wave function for the bound states to be finite and zero, respectively, at these two points. Therefore we have to ensure that $b_H$ has one of the special values for this situation to occur. Since in our application $b_H$ is expressed in terms of $\mu$ (Table II), satisfying this condition will determine the allowed values of $\mu$ and therefore of the eigenvalue $\lambda$ through Eq. (3.15).

Equation (D3) has the form

$$p_j R_j - q_j + \frac{r_j}{R_{j-1}} = 0,\ j \geqslant 1, \quad \text{(D5)}$$

which can be turned around to

$$R_{j-1} = \frac{r_j}{q_j - p_j R_j},\ j \geqslant 1. \quad \text{(D6)}$$

We obtain the definitions of $p_j$, $q_j$, and $r_j$ from Eq. (D3), for $j \geqslant 1$:

$$p_j = \nu\left(1+\frac{1}{j}\right)\left(1+\frac{\gamma}{j}\right), \quad \text{(D7)}$$

$$q_j = \nu + 1 + \frac{1}{j}[\gamma+\delta-1+(\alpha+\beta-\delta)\nu] - \frac{b_H}{j^2}, \quad \text{(D8)}$$

$$r_j = \left(1+\frac{\alpha-1}{j}\right)\left(1+\frac{\beta-1}{j}\right). \quad \text{(D9)}$$

The $j=1$ case of Eq. (D6) is $R_0=r_1/(q_1-r_1R_1)$, and we already know $R_0=c_1/c_0=-b_H/(\gamma\nu)$. Further we have the requirement of "augmented convergence" (Ref. [10], p. 77), that $\lim_{j\to\infty}|R_j|=1/\nu<1$. By iterating Eq. (D6), we expand it into a continued fraction, and we obtain the equation that is to be solved for $\mu$:

$$0 = \frac{b_H}{\gamma\nu} - \frac{-r_1}{q_1-}\frac{p_1 r_2}{q_2-}\frac{p_2 r_3}{q_3-}\frac{p_3 r_4}{q_4-}\cdots. \quad \text{(D10)}$$

At this point we introduce the small part of the theory of continued fractions [48] that we need. The generic continued fraction has the form

$$f = b_0 + \frac{a_1}{b_1+}\frac{a_2}{b_2+}\frac{a_3}{b_3+}\cdots. \quad \text{(D11)}$$

If this expression is truncated at the $n$th level, the result is called the $n$th convergent, and it can be simplified into an ordinary fraction

$$f_n = b_0 + \frac{a_1}{b_1+}\frac{a_2}{b_2+}\frac{a_3}{b_3+}\cdots\frac{a_n}{b_n+0} = \frac{A_n}{B_n}. \quad \text{(D12)}$$

The numerator and denominator in this expression are calculated recursively from

$$A_n = b_n A_{n-1} + a_n A_{n-2},\ B_n = b_n B_{n-1} + a_n B_{n-2}, \quad \text{(D13)}$$

and the initial values $A_{-1}=1$, $A_0=b_0$, $B_{-1}=0$, and $B_0=1$. We compare Eqs. (D10) and (D11) and obtain

$$b_0 = \frac{b_H}{\gamma\nu}, \quad \text{(D14)}$$

$$a_j = -p_{j-1}r_j = \nu\left(1+\frac{1}{j-1}\right)\left(1+\frac{\gamma}{j-1}\right)\left(1+\frac{\alpha-1}{j}\right)\left(1+\frac{\beta-1}{j}\right), \tag{D15}$$

$$b_j = q_j, \tag{D16}$$

for $j \geq 1$; we define $p_0 = -1$ for consistency.

We now have the formulas we need to determine the allowed values of $\mu$ numerically.We substitute for all parameters $\alpha$, $\beta$, $\gamma$, $\delta$, $b_H$ from the first and second line of Table II. (The results from the third and fourth lines duplicate those from the first two lines.) For a given value of the shape parameter $a$, $\nu$ is determined from Eq. (3.6), so the only unknown is $\mu$. We truncate the continued fraction at some $n$th level where we can accurately replace $R_n$ by its required limit $1/\nu$. Then, by use of Eq. (D13), the truncated version of Eq. (D10) becomes a high-order polynomial equation in $\mu$, and we need to determine its roots. We wrote a computer algebra program to determine these roots from three consecutive convergents $f_n$, $f_{n+1}$, and $f_{n+2}$. We found that taking $n$ equal to 8, 9, or 10, we obtained agreement among the three convergents to at least 10 decimal places. This agreement deteriorated to about 5 decimal places for $\nu \to 1$, which is $a \to 2/9$; however, we already know the answer in that limit from other considerations (Sec. III C).

From the allowed values of $\mu$ we obtain the eigenvalues $\lambda$, and then the allowed values for the squares of the small oscillation frequencies $\omega_i^2$. The results for $\omega^2$ are shown in Fig. 4 and are discussed in Sec. III D.

## APPENDIX E: FREQUENCY RATIOS

To calculate the frequency ratio in Eq. (6.17), we use techniques employed by Trullinger and de Leonardis [49] to analyze the small oscillation spectrum about the kink solution of a double-quadratic system and by Büttiker and Landauer [32] to calculate the kink-antikink nucleation rate for an overdamped biased sine-Gordon chain. The potential energy $v(x)$ [Eq. (3.10)] in our Schrödinger equation approaches zero exponentially for $|x| \to \infty$. Therefore we imagine a large length $L$ such that the region where $v(x)$ is appreciably different from zero is contained within the interval $-L/2 < x < L/2$; eventually, we want $L \to \infty$. We have previously noted that $v(x)$ is an even function of $x$ and that we can choose eigenfunctions that are either even or odd functions.

For $x \approx \pm L/2$, the particle is essentially free, so the even ($e$) and odd ($o$) eigenfunctions have the form

$$\phi^{(e,o)}(x) \underset{x \approx \pm L/2}{\to} C_k^{(e,o)} \begin{bmatrix} \cos \\ \sin \end{bmatrix} \left( kx \pm \frac{1}{2}\Delta^{(e,o)}(k) \right). \tag{E1}$$

[The upper and lower elements in the array are the ($e$) and ($o$) cases, respectively. In addition, the upper and lower signs go together. $C_k^{(e,o)}$ is a normalization constant.] To count the states, we impose periodic boundary conditions (PBC's) on the interval $-L/2 < x < L/2$ and obtain the condition

$$k\left(x+\frac{L}{2}\right) + \frac{1}{2}\Delta^{(e,o)}(k) - \left[ k\left(x-\frac{L}{2}\right) - \frac{1}{2}\Delta^{(e,o)}(k) \right] = kL + \Delta^{(e,o)}(k) = 2\pi n^{(e,o)}, \tag{E2}$$

where $n^{(e,o)} = 1, 2, 3, \ldots$ .

We use the WKB approximation [50] to obtain the phase shift. For familiarity we revert to textbook quantum mechanics notation for a few equations, where the Schrödinger equation is

$$-\frac{\hbar^2}{2M}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi. \tag{E3}$$

With $V(x) = V(-x)$, the even and odd WKB wave functions are

$$\psi^{(e,o)}(x) = \frac{C^{(e,o)}}{\sqrt{\frac{2M}{\hbar^2}[E - V(x)]}} \times \begin{bmatrix} \cos \\ \sin \end{bmatrix} \left\{ \int_0^x dx' \sqrt{\frac{2M}{\hbar^2}[E - V(x')]} \right\} \tag{E4}$$

($C^{(e,o)}$ is a normalization constant). The total phase shift across the periodicity interval is

$$\int_0^{L/2} dx \sqrt{\frac{2M}{\hbar^2}[E - V(x)]} - \int_0^{-L/2} dx \sqrt{\frac{2M}{\hbar^2}[E - V(x)]} = 2\int_0^{L/2} dx \sqrt{\frac{2M}{\hbar^2}[E - V(x)]}. \tag{E5}$$

We equate this to the total phase change in Eq. (E2) and obtain

$$kL + \Delta^{(e,o)}(k) = 2\pi n^{(e,o)}(E) = 2\int_0^{L/2} dx \sqrt{\frac{2M}{\hbar^2}[E - V(x)]}. \tag{E6}$$

We have written $n^{(e,o)}(E)$ here because it is the number of states up to energy $E$. In the WKB approximation, this number is the same for the even- and odd-parity states. The derivative with respect to $E$ of the number of states is the DOS. The total density of states is the sum of the even and odd cases, so

$$\rho_b(E) = \frac{2M}{\pi\hbar^2}\int_0^{L/2} dx \frac{1}{\sqrt{\frac{2M}{\hbar^2}[E - V(x)]}}. \tag{E7}$$

We compare Eq. (E3) with Eq. (2.22) and see that we should replace

$$E \to \frac{\omega^2}{a} - 1, \quad \frac{2M}{\hbar^2} \to \frac{a}{c_0^2}, \quad V(x) \to -\frac{4}{a}u_b^2(x) + \frac{15}{2a}u_b^4(x). \tag{E8}$$

Finally, we change the integration variable to $y$ from Eq. (3.5), introduce the eigenvalue $\lambda$ from Eq. (3.7) and the function $v(y)$ from Eq. (3.10), to write the DOS as

$$\rho_b(\lambda) = \frac{1}{\pi}\int_0^{\sqrt{a}L/(2c_0)} dy \frac{1}{\sqrt{\lambda - v(y)}}. \tag{E9}$$

The DOS for small oscillations about the metastable minimum is obtained by omitting the function $v(y)$, so

$$\rho_{ms}(\lambda) = \frac{1}{\pi}\int_0^{\sqrt{a}L/(2c_0)} dy \frac{1}{\sqrt{\lambda}} = \frac{L}{2\pi}\frac{\sqrt{a}/c_0}{\sqrt{\lambda}}. \tag{E10}$$

We substitute Eqs. (E9) and (E10) into Eq. (6.17) for $\ln(Q^2/a^2)$, and we take the thermodynamic limit $L\to\infty$, which also removes $c_0$ from this function. Then we interchange the order of integration, so that

$$\ln(Q^2/a^2) = \frac{1}{\pi}\int_0^\infty dy \int_0^\infty d\lambda \ln(1+\lambda)\left[\frac{1}{\sqrt{\lambda}} - \frac{1}{\sqrt{\lambda - v(y)}}\right]. \tag{E11}$$

The integral on $\lambda$ can be done analytically [51]; the result depends on whether $v(y)$ is less than or greater than $-1$. For $a<10/49$, there is one solution to the equation $v(y)=-1$, and for $10/49<a<2/9$, there are two. The integral on $y$ must be broken into intervals depending on the magnitude of $v(y)$, and then those integrals must be evaluated numerically.


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