Diffusion controlled initial recombination

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This work addresses nucleation rates in systems with strong initial recombination. Initial (or ''geminate'') recombination is a process where a dissociated structure (anion, vortex, kink, etc.) recombines with its twin brother (cation, antivortex, antikink) generated in the same nucleation event. Initial recombination is important if there is an asymptotically vanishing interaction force instead of a generic saddle-type activation barrier. At low temperatures, initial recombination strongly dominates homogeneous recombination. In a first part, we discuss the effect in one-, two-, and three-dimensional diffusion controlled systems with spherical symmetry. Since there is no well-defined saddle, we introduce a threshold which is to some extent arbitrary but which is restricted by physically reasonable conditions. We show that the dependence of the nucleation rate on the specific choice of this threshold is strongest for one-dimensional systems and decreases in higher dimensions. We also discuss the influence of a weak driving force, and show that the transport current is directly determined by the imbalance of the activation rate in the direction of the field and the rate against this direction. In a second part, we apply the results to the overdamped sine-Gordon system at equilibrium. It turns out that diffusive initial recombination is the essential mechanism which governs the equilibrium kink nucleation rate. We emphasize analogies between the single particle problem with initial recombination and the multidimensional kink-antikink nucleation problem. [S1063-651X(98)10008-9]

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I. INTRODUCTION

The purpose of this work is to support our approach to the nucleation problem of kinks and anti-kinks in the overdamped sine-Gordon chain at equilibrium [1] by investigating closely related problems which are dominated by initial (or ''geminate'') recombination processes. Initial recombination is a process where a dissociated structure (anion, vortex, kink, etc.) recombines with its twin brother (cation, antivortex, antikink) generated in the same nucleation event [2–6]. Our theory of kink-antikink nucleation [1] leads in the thermal equilibrium state of the sine-Gordon chain to an activation rate proportional to $\exp(-2E_k/kT)$, with an activation energy of twice the equilibrium kink energy E_k. This can be compared with earlier work [7] which predicts a rate proportional to $\exp(-3E_k/kT)$. This significant difference in the nucleation rates is a consequence of initial recombination of kink-antikink pairs. Although our discussion presents a clear physical picture, our results are apparently not obvious and have already given rise to discussions in the literature [8,9]. It is therefore necessary to further support and explain more deeply the point of view and the approach taken in Ref. [1].

Usually, nucleation theory [10] (for reviews, see Refs. [11,12]) is associated with the decay of a metastable state across an activation barrier. A simple picture is a Brownian particle which has to overcome a barrier in order to leave the region of attraction of a potential well [see Fig. 1(a)]. One of the main tasks of nucleation theory is the evaluation of the current flow out of the well for a given density of particles in the well. The relevant time scale of such an activated process is dominated by an inverse Arrhenius factor $\exp(E_0/kT)$, where E_0, k, and T denote the activation energy, the Boltzmann constant, and the temperature, respectively. The nucleation rate is then proportional to the Arrhenius factor. The proportionality constant is in the center of interest in many works, and depends strongly on the shape of the potential and on the strength of the damping of the Brownian particle.

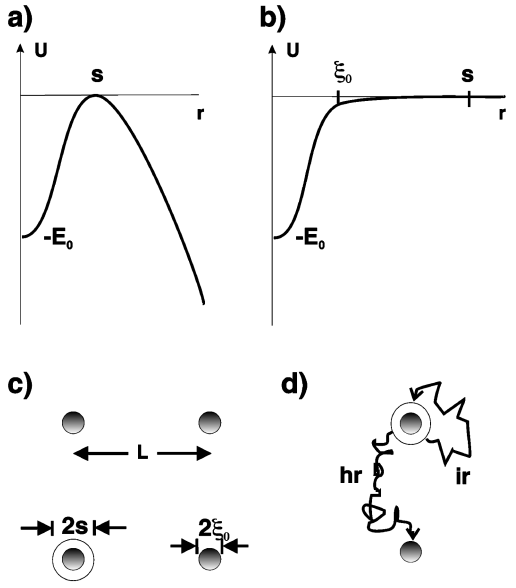

FIG. 1. (a) Potential well with an activation barrier at $r=s$ and with an activation energy E_0. (b) Potential well without a barrier maximum, but with a flat region; this case has to be treated by introducing a threshold point s. (c) Lattice of potential wells with distance L. (d) Typical traces of initial recombination (ir) and homogeneous recombination (hr).

In the present work we emphasize the particularly interesting problem of nucleation and recombination in systems with an asymptotically ''flat saddle'' [see Fig. 1(b)]. We will consider activation out of a well onto a region where the potential converges fast to a constant value, without crossing a barrier with a maximum. Except for a few remarks on the underdamped limit, we will restrict ourselves to strongly damped systems. This corresponds to a diffusion in configuration space on the flat saddle region. Furthermore we will allow a very slow drift due to a weak external driving force.

The main difference from the usual nucleation across a saddle with a well-defined maximum consists in an enhanced probability of backscattering into the well. Indeed, while there the particle is driven away by the deterministic force once the barrier maximum is traversed, the particle on a flat saddle executes a diffusive motion leading to a large probability of falling back into the original well. This process corresponds to initial recombination in generation-recombination kinetics and is in contrast to homogeneous recombination. The homogeneous recombination rate is proportional to the density of wells, and is much smaller than the rate of initial recombination for a diluted well density. The processes are illustrated in the lower part of Fig. 1.

In the following we mention some examples of initial recombination. The most prominent one appears in dissociation theory of diffusion controlled chemical reactions [3]. In his 1938 paper [2], Onsager determined the probability of recombination of a pair of ions after a given initial separation r. It is well known that, despite the long-range nature of the Coulomb force, there is a finite escape probability in three dimensions even at zero external driving force. Onsager gives for the probability of escape $\exp(-r_o/r)$, where $r_o=q_1q_2/(4\pi\epsilon_r\epsilon_0 kT)$ is called the Onsager radius, $q_{1,2}$ denote the charges of the anion and cation, and $\epsilon_r\epsilon_0$ is the dielectric permeability of the medium. While for small initial distances r the attractive Coulomb interaction leads to strong initial recombination, diffusion dominates Coulomb interaction for r larger than the Onsager radius, which leads to a large escape probability. It is clear that in a dilute electrolyte and if the dissociation process is due to thermal nucleation, initial recombination dominates homogeneous recombination. This has strong consequences on the free ion density in a superimposed electric field, since initial recombination is very sensitive to an external force. Note that in a flat potential, i.e., if $r_o=0$, Onsager's result predicts a vanishing initial recombination rate. We will show below that this is characteristic for a three-dimensional system, and it will be different for lower dimensions.

A two-dimensional example is the two-dimensional (2D) Coulomb gas. Here the force vanishes proportional to $1/r$, which leads to a logarithmically increasing potential. Though the potential is not ''flat,'' this case is particularly interesting (see, e.g., Ref. [13]). Dissociation in the 2D Coulomb gas describes, for instance, vortex-antivortex nucleation in superfluid helium films. An important feature of this system is that there is an unbinding transition of pairs at a critical temperature. At low temperatures the escape probability vanishes, whereas above a critical temperature it is finite. This transition, which is known as the Kosterlitz-Thouless transition, can be seen as a consequence of strong initial recombination which inhibits free excitations below the critical temperature [4]. We mention that there is no simple single-particle picture of the Kosterlitz-Thouless transition, since screening of the excitations play a major role.

Initial recombination in one-dimensional systems is faced, e.g., in photoelectric carrier generation in 1D semiconducting polymers [5]. Haberkorn and Michel-Beyerle [6] considered electrons which are photogenerated close to an electrode in a one-dimensional conductor, including the image force at the electrode. In particular, they discussed the relation between the total current due to a weak external force, and the ''nucleated'' current. We will take up these results below,

Note that the listed examples are all controlled by an interaction force rather than by diffusion alone. In this paper, however, we emphasize diffusion controlled, i.e., entropy driven, initial recombination. This requires that the force be short ranged. Short- range forces occur, e.g., between kinks or domain walls in (quasi-) one-dimensional systems. A kink-antikink interaction potential is often a monotonously increasing function of the separation, and becomes exponentially flat for large separations [14].

The paper is organized as follows. In order to fix the notation and for later comparison, in Sec. II we briefly review some standard results of the theory of nucleation across a barrier. In Sec. III, we discuss the nucleation across flat saddles, including the effect of a weak force, and the initial recombination time. In Sec. IV, diffusion controlled initial recombination is illustrated for the example of equilibrium kink nucleation.

II. ESCAPE ACROSS A BARRIER

In the following we consider the motion of a particle in d dimensions with coordinate $\vec{r}$, mass m, damping constant γ, and in a potential $U(\vec{r})$. Of course, the particle coordinate vicariously stands for relevant variables of a rather large class of systems (chemical reaction variables, ion separation distance, liquid droplet radius, magnetization, etc.). Throughout this paper, we assume that the potential U has a minimum at $\vec{r}=0$, and depends only on the distance $r=|\vec{r}|$. In a one-dimensional system ($d=1$), this means that $U(r)$ is an even function of the coordinate r. The particle is furthermore coupled to a heat bath of temperature T. The equation of motion for $\vec{r}$ is a Langevin equation with a white noise force [15]. Equivalently, the system can be described by Kramers equation for the phase-space probability density $f(\vec{r},\vec{v},t)$, where $\vec{v}$ is the velocity of the particle (for our purposes we may use the velocity instead of the momentum). Below, we almost always consider the strongly damped case in which Kramers equation reduces to the Smoluchowski equation

$$\partial_t P+\nabla\vec{j}=0, \tag{1}$$

which is a continuity equation for the probability density $P=\int d^dv\, f$ in configuration space. The probability current $j=\int d^dv\, v f$ is given by

$$\vec{j}=-\frac{1}{m\gamma}(P\nabla U+kT\nabla P), \tag{2}$$

where the Einstein relation $D=kT/m\gamma$ between diffusion constant D and damping constant γ is related to local equilibrium.

The nucleation rate $J_{\rm nuc}$ can be defined as follows. First, one has to find a stationary solution of Kramers equation which is normalized in the well. Outside the well, this solution has to satisfy appropriate boundary conditions. Usually, absorbing boundary conditions are applied. Then the current crossing the boundary is the nucleation rate. This approach has the advantage that the determination of the nucleation rate is reduced to the solution of a stationary (time-independent) problem.

In the remaining part of this section, we recall some results for one-dimensional systems and for saddles which are not flat in the above mentioned sense. Furthermore, we restrict the discussion to low temperatures, i.e., $kT \ll E_0$. For moderate-to-strong damping, for a quadratic saddle at $r=s$, Kramers found an analytical result which reduces in the strong damping limit to the Smoluchowski rate

$$J_{\rm nuc}=2\ \frac{\omega_0\omega_S}{2\pi\gamma}\exp(-E_0/kT). \tag{3}$$

The rate depends on the Arrhenius factor $\exp(-E_0/kT)$, on the damping constant γ, and on the curvatures at the minimum and at the saddle, $\omega_0=\sqrt{\partial_r^2 U(0)/m}$ and $\omega_S=\sqrt{|\partial_r^2 U(s)|/m}$, respectively. The factor 2 in Eq. (3) occurs because the symmetry of the one-dimensional potential implies two equivalent paths of escape from the well. In the weak damping limit ($\gamma\to 0$), Kramers' moderate-to-strong damping result yields the transition state (TST) rate

$$J_{\rm TST}=2\frac{\omega_0}{2\pi}\exp(-E_0/kT). \tag{4}$$

This result is wrong since thermal equilibrium is assumed in the well which is no longer the case at very low damping. An appropriate (slow) variable is then the action variable I (or the energy E). By an averaging over the fast angle variable, Kramers therefore derived a diffusion equation in action space. A solution of the nucleation problem in this space yields the true rate in the $\gamma\to 0$ limit:

$$J_{\rm nuc}=\gamma\frac{\omega_0 I_S}{2\pi kT}\exp(-E_0/kT). \tag{5}$$

Here I_S is the action of the separatrix trajectory at the saddle in phase space. We mention that result (5) remains also valid for the ''flat saddle'' in Fig. 1(b), since at $\gamma\to 0$ the particle escapes ballistically, i.e., without backscattering in the region with constant potential.

Rates (3) and (5) are the leading order results in $1/\gamma$ and γ, respectively. The crossover between these limits is known as the Kramers turnover problem. Renewed attention to this problem followed Refs. [16,17] which investigated the leading corrections to Eq. (5) and provided computational results illustrating the turnover. A particularly elegant approach to this problem was put forth in Refs. [12,18], and independently in Refs. [19,20] based on boundary layer theory. Later it was noticed that the problem can be solved over the entire turnover region by normal mode analysis [21]. We expect that for the flat saddle, the first correction term to Eq. (5) is strongly changed as compared to the quadratic saddle. In particular, there should be a strong dependence on the length of the diffusion region. In the present work, however, we consider the strongly damped case, or corrections to this case for finite but small $1/\gamma$. To find the corrections, we will use a result of boundary layer theory.

III. ESCAPE ACROSS A FLAT POTENTIAL REGION

We again consider a symmetrical potential well. For decreasing $r<\xi_0$, the potential is assumed to drop strongly and monotonously to its minimum value $-E_0$ at $r=0$. For $r>\xi_0$, it is assumed to increase monotonously and to converge quickly to zero. Here ξ_0 is a characteristic half-width of the well defined by the specific physical problem under consideration (see, e.g., Sec. IV). A typical example is sketched in Fig. 1(b). As mentioned above, for the one-dimensional case $d=1$, we assume reflection symmetry, and in higher dimensions we assume a rotationally invariant potential, which allows us to confine all calculations to $r\geqslant 0$. On a large length scale L ($\gg\xi_0$), we assume a periodic lattice of such wells. A two-dimensional sketch is shown in Fig. 1(c). Since there is no activation barrier, we introduce a fictitious boundary which separates bound states and free states. We define the occurrence of a nucleation event as the escape of the particle from the region $r<s$. Initial recombination denotes recombination with the original well, while we define here homogeneous recombination as capture by a neighboring well [Fig. 1(d)]. We emphasize that homogeneous recombination and initial recombination differentiate histories of particles with separations larger than s. A homogeneous recombination event is thus represented by a trajectory that starts from s and ends up at a different well, whereas initial recombination is represented by a trajectory that starts from s and after excursion in the flat potential region returns to the initial well. Initial recombination, like homogenous recombination, thus refers to particles that have completely dissociated. The only difference is their different subsequent history due to diffusive motion.

In order to determine the nucleation rate, we consider first a single well. The bare potential $U(r)$ does not exhibit a saddle and the particle ''feels'' an attracting force which, however, becomes (exponentially) small with increasing distance from the well. Once the particle is far enough away, it behaves thus purely diffusive and must be considered to be free. As in standard nucleation theory, the solution of the Kramers problem must obey absorbing boundary conditions outside the well. The introduction of the point $r=s$ on the flat region where these boundary conditions are applied defines the size of a fictitious saddle separating the bound state from the free states. The exact location of this point is not determined due to local translational invariance in the region of constant potential. However, besides satisfying $L\gg s\gg\xi_0$, it should be fixed by physical conditions. A typical example of an experimental condition which provides a certain value of s is the finite resolution of an instrument which counts the free particles [9].

To calculate the nucleation rate, we solve the stationary Smoluchowski equation (1) in radial coordinates. Due to rotational symmetry there is no dependence on angle coordi-

nates for $d>1$. With an ansatz $P(r)=\beta(r)\exp[-U(r)/kT]$ for the probability density, one finds, from Eq. (1) for the radial current density in d dimensions,

$$j_r=-D\ \exp[-U(r)/kT]\partial_r\beta(r)=\frac{C}{r^{d-1}}. \tag{6}$$

Here C has to be determined, and is related to the nucleation rate by $J_{\rm nuc}=a_dC$ with $a_1=2$, $a_2=2\pi$, and $a_3=4\pi$. The density is assumed to be normalized

$$\int_0^s P(r)a_dr^{d-1}dr=1, \tag{7}$$

and to satisfy the linear, homogeneous, and mixed boundary conditions at s [22]:

$$x_m\partial_rP\big|_s+P\big|_s=0. \tag{8}$$

Some comments concerning this boundary condition are in order (see, e.g., Ref. [3]). First, $x_m=\alpha\sqrt{D/\gamma}$ is the Milne length which is a measure for the nonequilibrium boundary layer at an absorbing boundary. Indeed, $x_m\propto\sqrt{kT/m}/\gamma$ can be interpreted as the mean free path of a particle with thermal velocity. We mention that the first term in Eq. (8) can be understood as a correction obtained from a Taylor expansion to first order with respect to x_m. In one dimension, $\alpha=\zeta(-\frac{1}{2})\approx1.46$. In higher dimensions, α is changed (e.g., due to the finite curvature of the boundary), but here we are not interested in details concerning this problem, and we will use α as a given parameter. In the limit $\gamma\to\infty$, an absorbing boundary at s implies $P(s)=0$. On a microscopic length scale, the boundary condition (8) describes the solution asymptotically far away from the absorbing boundary, $r<s-x_m$. The boundary layer itself ($s-x_m<r<s$) shows a more complicated structure [22,23]. Hence Eq. (8) cannot be used if x_m is of the order of s, or if the boundary layer leaks into the well. The mixed boundary condition (8) serves only to investigate how the results presented below change as we depart from the regime of strongly damped motion; it should be clear that, for weak friction, it is not sufficient to consider the Smoluchowski equation but instead one has rather to use the full Kramers equation.

Let us now continue with the derivation of the nucleation rate. Integration of Eq. (6) together with Eqs. (7) and (8) yields

$$J_{\rm nuc}=D\left[\int_0^s r^{d-1}dr\ e^{-U(r)/kT}\left(\frac{x_ms^{1-d}}{e^{-U(s)/kT}}+\int_r^s\frac{z^{1-d}dz}{e^{-U(z)/kT}}\right)\right]^{-1}. \tag{9}$$

Alternatively, we could derive this result by evaluating the mean first passage time (see, e.g., Ref. [11]) of a particle starting at $r=0$ and reaching $r=s$, with appropriate boundary conditions.

Despite rotational symmetry of the saddle manifold for $d>1$, the rate cannot be determined by using the volume of the symmetry group in the order-parameter ($\vec{r}$) space [24]. This works only for a saddle with a well-defined sharp maximum. We anticipate that the nucleation rate (9) depends in general on s. The discussion of the dependence of the nucleation rate on this parameter is our main goal. In the sequel the high- and low-temperature limits will be discussed separately.

A. High-temperature limit

For very high temperatures $kT\gg E_0$, the particle ''sees'' an overall flat potential and does not ''feel'' the well. From Eq. (9), one finds a rate

$$J_{\rm nuc}=\frac{D}{s^2}\frac{2d}{1+2(x_m/s)}. \tag{10}$$

In the high-friction limit this describes just the spatial diffusion out of a region $r<s$. In the low-friction limit, on the other hand, the rate is $dD/(sx_m)=\sqrt{kT/m}/s\alpha$. Although this result cannot be exact as discussed above, let us compare it with an estimate of the zero-friction result obtained directly from phase-space considerations. In the limit $x_m\gg s$, the probability density in phase space, $f(r,v)$, must be considered rather than the configuration space density $P(r)$. For a constant potential, we take $f=A\ \exp(-mv^2/2kT)$ for radial velocities pointing away from the well, and $f=0$ for velocities pointing toward the well. In the following, we restrict ourselves to the one-dimensional case. The density in configuration space ($r\geqslant0$) and the current density are $P=\int dv\,f=A\sqrt{\pi kT/2m}$ and $j=\int v\ dv\,f=kTA/m$, respectively. Normalization implies $P=1/2s$ and we find $J_{\rm nuc}=2j=(\sqrt{2/\pi})(\sqrt{kT/m})/s$. Up to a constant factor of order 1 this is in rather good agreement with the result derived from Eq. (10).

Let us briefly determine the recombination time τ_1 in the overdamped one-dimensional case. Due to equipartition at high temperatures, the ratio of free particles ($r>s$) to particles which are not free ($r<s$) is given by $N_{\rm free}/N_{\rm well}=(L-s)/s\approx L/s$. Now the total nucleation rate and the recombination rate balance each other, $N_{\rm well}J_{\rm nuc}=N_{\rm free}/\tau_1$. Using Eq. (10), this immediately yields the recombination time $\tau_1=Ls/2D$. In Sec. III C, we will discuss the recombination times more deeply.

We notice that in the high-temperature limit the assumption of a diluted gas of nucleated structures, i.e., the assumption $L\gg\xi_0$, breaks down in many physical applications. This is because L^{-d} is often a density of nucleated structures which is itself proportional to an Arrhenius factor, and becomes large at high temperatures. In that case, initial recombination and homogenous recombination can no longer be clearly separated.

B. Low-temperature limit

In this case, the d-dimensional probability density in the well is a normalized [see Eq. (7)] equilibrium distribution

$$P_0(r)=A_d\exp[-U(r)/kT], \tag{11}$$

with the normalization constant

$$A_d=\left(\frac{m\omega_0^2}{2\pi kT}\right)^{d/2}\exp(-E_0/kT). \tag{12}$$

The low-temperature nucleation rate is given by

$$J_{\rm nuc}=a_d A_d D\left(\int_{\xi_0}^{s} r^{1-d}dr+x_m s^{1-d}\right)^{-1}, \tag{13}$$

where ξ_0 is the size of the well. It is interesting, that in one space dimension ($d=1$), result (13) can be written in the form

$$J_{\rm nuc}=\frac{\sqrt{2\pi}}{\alpha}\frac{x_m}{s-\xi_0+x_m}J_{\rm TST}, \tag{14}$$

where $J_{\rm TST}$ is the transition state rate (4). Note that despite of the vanishing of x_m in the limit $m\to 0$, where the particle is overdamped, the rate remains finite since $J_{\rm TST}$ diverges. In the overdamped limit and for $\xi_0 \ll s$, the rate is proportional to $1/s$, and can be expressed in the form

$$J_{\rm nuc}=2\frac{\omega_0}{\gamma s}\sqrt{\frac{kT}{2\pi m}}\exp(-E_0/kT). \tag{15}$$

Equation (15) and its dependence on $1/s$ can be understood as follows. The probability that a particle reaches the flat portion of the potential at a point r ($\xi_0 \ll r \ll s$) is proportional to the equilibrium probability distribution function at this point. Since, according to our choice of the zero of energy, we have for $r \gg \xi_0$ a potential $U\equiv 0$, the equilibrium probability distribution is just given by the prefactor A_1 in Eq. (11) specified in Eq. (12). Diffusion over a distance s along the flat potential region in a medium with diffusion constant $D=kT/m\gamma$ reduces the probability by D/s. The current at a distance s is $J=A_1 D/s$. Since our potential is symmetric around $r=0$, a current of the same magnitude is also obtained for $r=-s$. Thus the total current is $J_{\rm nuc}=2A_1 D/s$, which is indeed just Eq. (15). Thus the $1/s$ dependence is a natural consequence of the flatness of the potential, and the fact that a particle can progress in this region only via diffusion. Equation (15) is the central result of this work. According to Eq. (15), the characteristic decay time scales linearly with s. In Sec. IV, we show that the equilibrium nucleation reate of kinks has the same dependence on s.

For weak damping $x_m \gg s$, we find that $J_{\rm nuc}$ deviates from the transition state result only by a factor of 1.73. This (relatively small) deviation is due to the above mentioned fact that the inner structure of the boundary layer must be taken into account and cannot be described simply by a boundary condition. One finds exactly the transition state result by an appropriate matching of the probability density $P=A\sqrt{\pi kT/2m}$ (see the end of Sec. III A) to the part of solution (11) associated with right-moving particles ($r>0$). Hence our result has a behavior similar to Kramers' moderate-to-strong damping formula for the quadratic saddle. As mentioned, Eq. (11) is a wrong distribution at low damping since local equilibrium in the well is not established, and the nucleation rate at $\gamma\to 0$ is given by Eq. (5).

In two and three space dimensions, the rates can be expressed in the form

$$J_{\rm nuc}=\frac{\omega_0^2}{\gamma}\frac{\exp(-E_0/kT)}{\ln(s/\xi_0)+x_m/s} \tag{16}$$

and

$$J_{\rm nuc}=\frac{\omega_0^2}{\gamma}\sqrt{\frac{m\omega_0^2}{2\pi kT}}\frac{2\xi_0}{1-(\xi_0/s)+(\xi_0 x_m/s^2)}\exp(-E_0/kT), \tag{17}$$

respectively. In contrast to the one-dimensional case, the well size ξ_0 cannot be neglected for $d>1$. Moreover, in two dimensions the s dependence is logarithmically weak, and in three dimensions its influence can be neglected. We mention that a discussion of the result in the limit $\xi_0\to 0$ requires some care, since ξ_0, ω_0, and E_0 are usually not fully independent.

Furthermore, in $d=2$, and 3, neither ξ_0 nor s are necessarily equal to the usual transition state obtained by extremalization of the effective potential $kT\ln[r^{1-d}\exp(U/kT)]=U(r)-kT(d-1)\ln(r)$. In contrast to the usual quadratic saddle, it is not only the vicinity of this transition state which contributes to the integral in Eq. (9). It is a larger region around the transition state that counts, of which ξ_0 and s, respectively, are the lower and the upper boundaries of integration.

C. Lifetime of free particles

We return now to the periodic lattice of the wells sketched in Fig. 1(c). Each well can then be associated with a unit cell of volume $V_d=L^d$ much larger than the volume associated with bound particles ($\propto s^d$). At equilibrium and at low temperatures, $kT \ll E_0$, the ratio of particles in the well to free particles is given by $N_{\rm well}/N_{\rm free}\approx 1/V_d A_d$. In steady state, the generation rate $N_{\rm well}J_{\rm nuc}$ equals the recombination rate $N_{\rm free}/\tau_d$. The lifetime of free particles is thus given by

$$\tau_d=\frac{V_d A_d}{J_{\rm nuc}}. \tag{18}$$

For very strong damping and for $\xi_0 \ll s$, Eqs. (14)–(17) imply

$$\tau_1=\frac{Ls}{2D}, \tag{19}$$

$$\tau_2=\frac{L^2}{2\pi D}\ln\left(\frac{s}{\xi_0}\right), \tag{20}$$

$$\tau_3=\frac{L^3}{4\pi D\xi_0}. \tag{21}$$

In one dimension, the lifetime scales linearly with s, while the s dependence in higher dimensions is weak or negligible. The higher the dimension, the smaller the probability of reaching the original well by pure diffusion. This is related to a divergence of the lifetimes as ξ_0 vanishes. We also mention that Eq. (21) corresponds to the standard result in the theory of diffusion controlled reactions, which states that the rate per volume is given by $4\pi D\xi_0$ (see, e.g., Ref. [3]).

For the one-dimensional case, the lifetime can be calculated directly by solving the Smoluchowski equation (1) for a flat potential, for absorbing boundary conditions $P(0)=P(L)=0$, and for an injected current $j(s+0)-j(s-0)=j_{\rm nuc}$ at $r=s$. If $P(r)$ is normalized, the lifetime is then given by $1/j_{\rm nuc}$. One finds that recombination can be understood as a sum of two contributions, i.e., it holds $j_{\rm nuc}=j_s+j_h$, where $j_s^{-1}=Ls/2D$ is associated with Eq. (19) and $j_h^{-1}=L(L-s)/2D$ is associated with diffusion to the neighbor well.

Below, in the discussion of equilibrium kink nucleation, we will first calculate the lifetime independently from the nucleation rate and from equilibrium statistical mechanics. Then using both results for the nucleation rate and the lifetime, we will derive the equilibrium kink density and show agreement with the statistical mechanics result for the kink density.

D. Effect of a weak force

In this section we discuss the influence of an external weak force F on nucleation in one dimension and at low temperature. The potential $U(r)$ is now replaced by the new potential $U(r)-Fr$. We are interested in the response to leading order with respect to F. The saddle is still flat enough such that diffusion dominates the drift in the relevant region: $kT \gg Fs$. For finite F, the current to the left (j_-) and to the right (j_+) are no longer equal, and the nucleation rate is $J_{\rm nuc}=j_++j_-$. Interestingly, as we will show below, the transport current J_{trans} is determined by the imbalance of the forward nucleation j_+ and the backward nucleation j_-. To leading order in F, the transport current is thus given by

$$J_{\rm trans}=j_+-j_-. \tag{22}$$

The symmetry relation $U(r)=U(-r)$ implies $j_+(F)=j_-(-F)$, and $J_{\rm nuc}$ is an even function of F while $J_{\rm trans}$ is an odd function of F. We find

$$j_+=D\frac{\tilde{A}_1 F}{kT}[1-\exp(-Fs/kT)]^{-1}, \tag{23}$$

where $\tilde{A}_1$ is the normalization constant given by Eq. (12) with a renormalized frequency and an energy of the new minimum:

$$\tilde{\omega}_0=\omega_0\sqrt{1+\frac{U^{(4)}}{2m^3\omega_0^6}F^2}, \tag{24}$$

$$\tilde{E}_0=E_0\left(1+\frac{F^2}{2m\omega_0^2E_0}\right). \tag{25}$$

In Eq. (24), we defined $U^{(4)}\equiv\partial_r^4U|_0$. The nucleation current $J_{\rm nuc}$ and the total current $J_{\rm trans}$ can then be written in the form

$$J_{\rm nuc}=\frac{F\tilde{A}_1}{m\gamma}\coth\left(\frac{Fs}{2kT}\right), \tag{26}$$

$$J_{\rm trans}=\frac{F\tilde{A}_1}{m\gamma}, \tag{27}$$

respectively. This yields a relation between the two currents, $J_{\rm trans}=J_{\rm nuc}\tanh(Fs/2kT)$. A similar result has been derived in Ref. [6] for photogenerated currents. According to our assumptions, the results are valid in leading order with respect to F. An expansion gives

$$J_{\rm trans}=\frac{Fs}{2kT}J_{\rm nuc}. \tag{28}$$

Since the nucleation rate is proportional to s^{-1}, the total current is independent of s as it must be.

We now present two derivations to show that the transport current Eq. (22) is indeed just determined by the imbalance of the forward and backward nucleation rates. For weak driving forces the transport current is equal to the density of free carriers, $n_{\rm free}$, multiplied by their drift velocity $u=\mu F$,

$$J_{\rm trans}=un_{\rm free}=\mu Fn_{\rm free}. \tag{29}$$

As usual, the mobility and the diffusion constant are related via the Einstein relation $D=\mu kT$. The number of free carriers is determined by the balance of the generation of free particles and their recapture into a well, $J_{\rm nuc}=N_{\rm free}/\tau$ with $N_{\rm free}=Ln_{\rm free}$. Here $J_{\rm nuc}$ determines the frequency with which free particles are generated, and $N_{\rm well}\approx 1$. The lifetime τ which determines the recapture back into the well is a function of F. But, to leading order in F, the equilibrium lifetime Eq. (19) is all we need. Eliminating the density of free carriers and using the Einstein relation, we find $J_{\rm trans}=\mu F\tau J_{\rm nuc}/L=(Fs/2kT)J_{\rm nuc}$. This is in accordance with Eq. (28), and thus $J_{\rm trans}=j_+-j_-$ holds.

A second derivation of this result proceeds as follows. We still consider a periodic potential with period L and which is symmetric around the origin. It is sufficient to consider the range $0\leqslant r<L$. We view the transport current as a consequence of the source currents j_+ at $r=s$ and j_- at $r=L-s$. The wells act as particle absorbers. The solution to this problem is a superposition of solutions to two problems each with one source alone. The current which flows back from $r=s$ in the presence of the source j_+ is denoted by j_+^L, and the current which flows forward to the next well by j_+^R. Similarly, the source j_- alone leads to a current back into the well at $r=L$ denoted by j_-^R and a current into the well at $r=0$ denoted by j_-^L. The transport current is then given by

$$J_{\rm trans}=j_+^R+j_-^L. \tag{30}$$

Continuity of current requires

$$j_+=j_+^R-j_+^L,\quad j_-=j_-^R-j_-^L. \tag{31}$$

As we have seen already the source currents have the symmetry $j_+(-F)=j_-(F)$. The homogenous recombination currents j_+^R and j_-^L are related by symmetry according to $j_+^R(-F)=-j_-^L(F)$. On the other hand, the initial recombination currents are even functions of the field $j_+^L(-F)=j_+^L(F)$ and $j_+^R(-F)=j_+^R(F)$ and, moreover, they are equal in magnitude but differ in their sign,

$$j_+^L(F)=-j_-^R(F). \tag{32}$$

The initial recombination currents are maximal for $F=0$. With increasing F the recombination current j_+^L decreases because homogeneous recombination increases. Similarly, the initial recombination current $j_-^R(F)$ decreases because there are fewer carriers activated into the high energy region of the potential. Using Eqs. (30) and (31) we obtain $J_{\rm trans}=j_+-j_-+j_+^L(F)+j_-^R(F)$. But as we have seen the sum of the two initial recombination currents cancel one another, and thus $J_{\rm trans}=j_+-j_-$. Thus at low fields the difference of the two activation rates directly determines the transport current. This can also be shown by a direct calculation. The direct relationship of the rates j_+ and j_- to the transport current demonstrates that these are physically meaningful and useful quantities.

IV. EQUILIBRIUM KINK NUCLEATION

In this section we investigate the dynamics of a string of particles coupled to each other harmonically, and moving in a sinusoidal potential. The particles are subject to damping and noise, and might be subject to an external driving force. This model is known as the driven and damped sine-Gordon chain. It has a long history and due to its wide range of applicability, from kinks in surface steps on various materials to the motion of fluxons in long Josephson junctions, has been widely studied [11,14,25–35]. In the overdamped limit, which is of interest here, there are only two types of elementary excitations. There are small amplitude phononlike excitations and, more interestingly, highly nonlinear structures, called kinks or solitary structures, which describe the transition from one valley to another. In chemical physics, kinks are discussed in various polymers [36]. Our concern is the statistical mechanics of such a system, which we take to be so large that one can define a density of kinks and antikinks. Of interest is a theory of the thermal equilibrium nucleation of kink-antikink pairs, and particularly the role of initial recombination [1]. We show that a theory of equilibrium kink nucleation, i.e., for a vanishing external driving force, *must* take into account initial recombination.

At small temperatures the kink-antikink gas is diluted, and the kink density sets an upper length scale over which nucleation and annihilation processes have to occur. In the framework of equilibrium statistical mechanics, kinks and antikinks are regarded as free particles. Below we shall explain that at equilibrium the distance between a ''mathematically unbounded'' kink-antikink pair is infinitely large. Apparently, this seems to contradict the notion of a free kink in a finite system. For reasons of consistency, it is thus necessary to develop a picture of the nucleation and annihilation processes which permits essentially free diffusive motion during the lifetime of a kink.

The nucleation, dynamics, and recombination of kinks and antikinks in space-time is schematically illustrated in Fig. 1 of Ref. [1]. Out of equilibrium, in the presence of a strong force (see Fig. 1(a) of Ref. [1]), the kink and antikink are driven apart after a nucleation process (empty triangles) by the force, and eventually annihilate with an antikink and a kink originating from a different nucleation process (rectangles). This picture has to be qualitatively modified in the equilibrium case without force. As shown in Fig. 1(b) of Ref. [1], the diffusive motion of the free kinks gives them a strongly enhanced probability of initial recombination (closed loops). Neglecting the closed trajectories is inconsistent with the experimental definition of free kinks. Former works [7,34] (see also Ref. [11]) do not include the initial recombination processes and count only the negligibly small fraction of extended trajectories (see Fig. 1(b) of Ref. [1]) which describe homogeneous recombination. Consequently, these works arrive at a much too low nucleation rate with an activation energy $3E_k$ associated with a kink triple, instead of the pair energy $2E_k$. Hence these works predict an incomprehensible breaking of the kink-antikink symmetry. A further consequence is a mean kink lifetime proportional to $\exp(2E_k/kT)$ [7,34,35], whereas our theory leads to a kink lifetime proportional to $\exp(E_k/kT)$.

To be specific, let us consider now the overdamped sine-Gordon equation [27]

$$\gamma\partial_t\theta=-V_0\sin\,\theta+F+\kappa\partial_x^2\theta+\zeta, \tag{33}$$

which describes the dynamics of an order-parameter field (a string of particles) $\theta(x,t)$ in a periodic potential of amplitude V_0, and with a coupling constant κ. Unless otherwise stated, the force F is set to zero. We assume periodic boundary conditions $\theta(\mathcal{L}+x,t)=\theta(x,t)$, where $\mathcal{L}$ is the sample length which exceeds every other relevant length scale of the problem (except the diverging size of the mathematical critical nucleus). Furthermore, ζ denotes a weak white noise force associated with the temperature T, i.e., with zero mean $\langle\zeta\rangle=0$ and the correlation function $\langle\zeta(x,t)\zeta(\tilde{x},\tilde{t})\rangle=2\gamma kT\delta(x-\tilde{x})\delta(t-\tilde{t})$. The uniform, stationary, and linearly stable states are given by $\theta_{s,l}=2l\pi$ (Peierls valleys) with integer l, and have equal energies. There exists an energy functional $E[\theta]$, such that Eq. (33) can be rewritten in the form $\gamma\partial_t\theta=-\delta E[\theta]/\delta\theta$. For a weak finite force, two adjacent Peierls valleys are separated in function space by a saddle which corresponds to a kink-antikink pair. A kink $\theta_k(x-x_0)$ centered at x_0 connects a Peierls valley $\theta_{s,l}$ with its neighbor $\theta_{s,l+1}$. An antikink is reversely defined by $\theta_a=\theta_k(-x+x_0)$. A kink-antikink pair at location x_0 and with a (not too small) separation r can be written approximately as $\theta_N(x)=\theta_k(x-x_0+r/2)+\theta_k(-x+x_0+r/2)-2\pi(l+1)$. In the presence of a weak force F, the mathematically exact saddle point of the energy functional corresponds to a pair with a separation $\xi=\xi_0\ln(V_0/F)$ where $\xi_0=\sqrt{\kappa/V_0}$ is now the kink size. In the equilibrium limit where $F\to0$, the separation ξ exceeds the inverse kink density n^{-1} or even the system length $\mathcal{L}$. In this case, the mathematically exact critical nucleus has no physical meaning. In order to overcome the problem of the large critical nucleus, we introduce an effective critical nucleus with a separation s of the kink and the antikink which is larger than a kink width but much smaller than an average equilibrium separation $L\equiv n^{-1}$ of kinks. The effective critical nucleus corresponds to the flat barrier with size s, in analogy to the effective saddle discussed in the previous sections.

A. Nucleation rate

We derive now the kink nucleation rate per length, $J_{\rm nuc}$. Note that, due to the periodic array of Peierls valleys, kink-antikink and antikink-kink excitations are equivalent. If the

nucleation rate of the former and the latter are denoted by j_+ and j_-, respectively, the rate becomes $J_{\rm nuc}=j_++j_-$. Of course, at equilibrium it holds $j_+=j_-$. The presence of spatial degrees of freedom requires a multidimensional Kramers theory [24]. The relevant coordinate is the kink-antikink separation r which can be associated with a quasi-Goldstone mode, besides the usual translational Goldstone mode of the pair. The quasi-Goldstone mode is $\delta\theta_N/\delta r=\theta_k'(x-x_0+r/2)/2+\theta_k'(-x+x_0+r/2)/2$ associated with an infinitesimal variation of r. The (orthogonal) Goldstone mode associated with an infinitesimal displacement δx_0 of the pair is $\delta\theta_N/\delta x_0=\theta_k'(-x+x_0+s/2)-\theta_k'(x-x_0+s/2)$.

The stationary Fokker–Planck equation associated with the Langevin equation (33) is solved in a way analogous to that in Sec. III [1]. Degrees of freedom which are transverse to the two Goldstone modes can be integrated out by Gaussian integration [30]. The rate per length of a kink-antikink pair then becomes [1]

$$j_+=\frac{1}{L}\frac{\tilde{Z}_N}{\tilde{Z}_s}\frac{\int_0^{\eta_1(L)}d\eta_1}{\int_0^{\eta_0(s)}d\eta_0}\exp(-2E_k/kT). \tag{34}$$

One concludes an activation energy $E_0=2E_k$, where $E_k=8\sqrt{\kappa V_0}$ is the equilibrium kink energy [30]. The variables η_0 and η_1 are the orthonormal-mode coordinates which belong to the kink-separation mode and to the translational mode, respectively. It holds that

$$d\eta_0^2=dr^2\int(\delta\theta_N/\delta r)^2dx,\quad d\eta_1^2=dx_0^2\int(\delta\theta_N/\delta x_0)^2dx. \tag{35}$$

Using the quasi-Goldstone and the Goldstone modes given above, one finds for the ratio of the integrals in Eq. (34) a value $2L/s$. The normalized partition function of the damped degrees of freedom at the saddle,

$$\frac{\tilde{Z}_N}{\tilde{Z}_M}=\frac{1}{2\pi}\sqrt{\lambda_0^M\lambda_1^M\prod_{n=2}^{\infty}\frac{\lambda_n^M}{\lambda_n^N}}, \tag{36}$$

contains the stability eigenvalues $\lambda_n^{M,N}$ of the metastable state (index M) and the critical nucleus (index N) with respect to perturbations with a decay (or a growth) $\propto\exp(\lambda t)$. The (quasi-) zero modes are excluded in the products. For a well-separated pair, Eq. (36) is the renormalized partition function of a kink-antikink pair without self-interaction, and is given by the square of the single kink partition function. Hence, $\tilde{Z}_N/\tilde{Z}_M=4\Gamma/2\pi$, where $\Gamma=V_0/\gamma$ [30]. The kink nucleation rate per length finally becomes

$$J_{\rm nuc}=2j_+=2\frac{4\Gamma}{\pi s}\exp(-2E_k/kT). \tag{37}$$

As discussed in Sec. III, the $1/s$ dependence is a consequence of the strong dependence of the rate on initial recombination events in one-dimensional systems.

B. Lifetime of kinks

In the following, we show that the result (37) is consistent with equilibrium statistical mechanics, which predicts an equilibrium kink density [30]

$$n_{\rm eq}=\sqrt{\frac{2V_0E_k}{\pi\kappa kT}}\exp(-E_k/kT). \tag{38}$$

In order to derive this result independently, we will calculate first the kink lifetime τ. By using the balance equation $J_{\rm nuc}\tau=n$, we obtain a kink density which has to be compared with Eq. (38).

The kink lifetime τ for a fixed antikink density n can be calculated with the help of a Langevin equation for the kink separation r. This Langevin equation follows from a projection of the sine-Gordon equation (33) onto the quasi-Goldstone mode discussed above. The Fokker–Planck equation, which is equivalent to the Langevin equation, in the stationary case reads $\partial_r(\tilde{F}P-\tilde{D}\partial_rP)=0$. Here we assumed a finite force F for later use. The effective force acting on the separation coordinate is given by $\tilde{F}=2\mu F$ with a mobility $\mu=2\pi\kappa/\gamma E_k$, and the diffusion constant is given by $\tilde{D}=2\mu kT/2\pi$ [29,30]. The values of $\tilde{F}$ and $\tilde{D}$ for the relative coordinate r are twice as large as for a single kink. Now we return to the case $F=0$. The stationary Fokker-Planck equation must be solved with a source at $r=s$, and with sinks at $r=0$ and $r=n^{-1}$. The source describes the nucleation of a pair, and the sinks model kink-antikink annihilation. The mean kink distance n^{-1} corresponds here to the well distance L introduced in Fig. 1(c) for one dimension.

Now we can proceed as in Sec. III C. Integration of the stationary Fokker–Planck equation leads to a piecewise constant current density, whereas the source implies a discontinuity of the current density of strength j_+ at s. The absorbing boundary conditions demand $P(0)=P(n^{-1})=0$. The lifetime τ is defined by the ratio of the total probability $\int dsP$ and the injected current j_+. One then finds immediately result (19) with L replaced by $1/n$, i.e.,

$$\tau=\frac{s}{2\tilde{D}n}. \tag{39}$$

The balance equation, together with Eq. (37) immediately implies the equilibrium density (38), which proves consistency with statistical mechanics, i.e., $n=n_{\rm eq}$.

As it must be, the stationary kink density (38) is independent of the specific value of s. The s dependence of the rate and of the lifetime can be illustrated in Fig. 1 of Ref. [1]. The kinks which are to be counted in $[0,\mathcal{L}]$ at a fixed time t must have been nucleated in a strip $(t-\tau,t)$ of width $\tau\propto s$. Since the number of counted kinks has to be independent of s, the density of generation events in this strip must be proportional to $1/s$. A variation of s affects only kinetic quantities like the time scale, but not thermodynamic equilibrium quantities like the kink density.

C. Effect of a weak force

In the presence of a weak force F, we expect a drift in the order-parameter field θ. Kinks and antikinks which pass a

given location with average velocity u and $-u$, respectively, each advance the field by 2π. Thus the average speed of the order-parameter field is

$$\langle \partial_t \theta \rangle = 2\pi u(n+m), \tag{40}$$

where m and n are the average kink and antikink densities. In our problem it holds $n=m$. To leading order in the field F, the velocity is simply determined by the kink mobility $u=\mu F$, and the kink density is determined by the equilibrium density. Thus to linear order in the force F the order parameter has a velocity [30]

$$\langle \partial_t \theta \rangle = 4\pi\mu F n_{\rm eq}. \tag{41}$$

We will rederive this result directly from the kink nucleation rates. As in the single-particle problem (28) of Sec. III D the transport current can be directly related to the asymmetry of the kink nucleation rates. The kink nucleation rate $J_{\rm nuc}$ is balanced by kink recombination $J_{\rm nuc}=n/\tau$. Here τ is the lifetime of kinks, which as we have seen is at low fields determined predominately by initial recombination and at $F=0$ is given by Eq. (39). Eliminating the kink density from Eq. (40), we obtain $\langle \partial_t \theta \rangle = 4\pi u \tau J_{\rm nuc}$. Now we find that the difference of the two nucleation currents is given by

$$j_+ - j_- = \frac{\tilde{F}s}{2\tilde{D}} J_{\rm nuc}. \tag{42}$$

To leading order in the field, it follows immediately that the average velocity of the displacement field is directly determined by the imbalance of the nucleation rates,

$$\langle \partial_t \theta \rangle = \frac{2\pi}{n_{\rm eq}}(j_+ - j_-). \tag{43}$$

This expression is equivalent to Eq. (41).

V. CONCLUSION

In this paper we have shown that diffusion controlled initial recombination strongly affects the activation rate in problems with flat potentials. The effect is particularly important in one-dimensional systems where the probability of diffusion back to the original well is very large. The absence of a well-defined barrier maximum requires the definition of an effective size of the barrier, i.e., a location where for the evaluation of the rate absorbing boundary conditions to the probability density are applied. In one-dimensional systems the time and, as a consequence, the inverse rate, scale linearly with this size.

Furthermore, we discussed equilibrium kink nucleation as an example where diffusion controlled initial recombination determines the kinetics. The effective saddle corresponds here to an effective critical nucleus. A certain arbitrariness of the nucleus size reflects the uncertainty of the notion of a free kink. A specific choice of this size, however, has to be related to physical considerations: obviously, it has to be larger than the kink width but much smaller than the mean kink distance. We have shown consistency of our results with equilibrium statistical mechanics. Furthermore, we have shown that the activation rates directly determine the transport current. Our work not only demonstrates that rates and lifetimes are useful quantities even if they depend explicitly on a length scale which separates free particles from bound particles. It also demonstrates that an evaluation of such rates is necessary to provide a physically meaningful discussion of problems in which diffusion controlled initial recombination plays a dominant role. Verification of the results presented here through computational work is difficult due to the long simulation times involved in nucleation problems. On the other hand, the many physical systems mentioned in the introduction to Sec. IV, to which the sine-Gordon theory applies, would certainly provide opportunities for the experimental investigations of equilibrium kink nucleation. We hope that the present work stimulates such experiments.

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