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The Uphill Turtle Race; On Short Time Nucleation Probabilities

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The short time behavior of nucleation probabilities is studied by representing nucleation as a diffusion process in a potential well with escape over a barrier. If initially all growing nuclei start at the bottom of the well, the first nucleation time on average is larger than the inverse nucleation frequency. Explicit expressions are obtained for the short time probability of first nucleation. For very short times these become independent of the shape of the potential well. They agree well with numerical results from an exact enumeration scheme. For a large number N of growing nuclei the average first nucleation time scales as $1/\log N$ in contrast to the long-time nucleation frequency, which scales as $1/N$. For linear potential wells closed form expressions are given for all times.

KEY WORDS: Nucleation time; activated process; first passsage time; escape rate.

1. INTRODUCTION

For large systems in a metastable state the rate of nucleation of droplets of the stable phase is proportional to system size, in other words the average time of formation of the first stable nucleus in a quasi-stationary metastable system may be expected to be inversely proportional to its size. At first sight this may convey the impression that one might shorten metastable lifetimes as much as one would like, just by making systems very large, but this is certainly too simplistic. On a large lake at a temperature slightly below freezing, a few ice crystals will be formed instantly, which subsequently will continue growing. But if the density of these crystals is very small it will still take a very long time for the lake to freeze over completely. In such cases the nucleation time may be defined as the average

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time it takes an arbitrary site in the system to become included in one of the growing stable regions. Quantitative descriptions of this scenario have first been given by Kolmogorov,(1) Johnson and Mehl,(2) and Avrami.(3) The main resulting effect is a reduction of the effective free energy barrier for nucleation by a factor of $d+1$, or slightly smaller, depending on the details of the growth dynamics, in d dimensions. Rigorous treatments of this theory may be found, e.g., in ref. 4.

Yet, for large, but not too large systems nucleation is brought about by the first nucleation core reaching supercritical size, which leads to a nucleation rate that is proportional to system size. The basic condition for this to occur is that the time needed for a supercritical nucleus to grow throughout the system is shorter than the inverse nucleation rate. But also in even larger systems the distribution of the first nucleation time may be of great interest, in case this event will cause an immediate dramatic change of the system. As an example of this, consider a condenser with plates separated by a dielectric in a metastable phase near a metal-insulator transition. The formation of a supercritical nucleus of the metallic phase immediately will lead to discharging of the condenser. Other examples of such phenomena could include explosive chemical reactions starting after the nucleation event (where we may generalize from nucleation resulting from phase transformation to basically any process requiring the crossing of some free energy barrier that is large compared to $k_B T$).

Especially for these cases it is important to realize that mostly, due to the initial preparation of the system, the average time to the first nucleation in fact is longer than the inverse of the asymptotic nucleation rate. The reason is that typically metastable states are formed by a rapid quench from a stable state, in which no large clusters of the new stable phase are present. The asymptotic state with a constant nucleation rate, on the contrary requires a size distribution for the nucleating clusters assigning non-zero probability (though small for large clusters) to clusters of any subcritical size.

This situation may be likened to an uphill turtle race where a large number of turtles is released at the bottom of a wide road leading up a hill, such that each of the turtles makes an independent random walk with a bias in the downhill direction. After a long time the turtles that have not reached the top yet will be distributed in some characteristic way along the slope, with most turtles near the bottom, but also some near the top, and an arrival frequency ν per turtle. The average time between subsequent arrivals at the top will be $(n\nu)^{-1}$, with n the number of remaining turtles. The average time of the first turtle to reach the top, however, will be much longer than $(N\nu)^{-1}$, with N the total number of turtles, due to the fact that initially all turtles are at the bottom. Roughly one may say the first arrival time contains a delay contribution, which is the time needed to set up the quasi-stationary asymptotic distribution starting from the initial state.

In this paper I will address the distribution of first nucleation times by approximating the nucleation process as a diffusion process in an abstract one-dimensional space, where the spatial coordinate indicates the sizes of growing nuclei. The next section gives the exact solution for a linear potential, corresponding to the case where the uphill road has constant slope. Section 3 treats the case of a general monotonic potential, Section 4 compares predictions to results obtained by numerically solving the uphill diffusion equation and the last section contains some concluding remarks.

2. EXACT SOLUTION FOR LINEAR POTENTIALS

Mean first passage times have been studied for a long time for diffusion in a potential well with the possibility of escape over a potential barrier.(5) In one dimension explicit expressions are known. For long times the probability of survival in the well without reaching the barrier approaches the exponential form

$$S^{\mathrm{long}}(t) = \exp[-\nu_{\mathrm{long}}(t-t_D)], \tag{1}$$

corresponding to an escape rate ν_{long}. The delay time t_D will depend on the initial distribution of the diffusor, but typically be much shorter than the average escape time $1/\nu_{\mathrm{long}}$. The probability distribution of survival in the well for a diffusor starting at some well-defined initial position has been studied much less. Yet the properties of this distribution, especially for a starting point at the bottom of the well are of great interest in many practical situations. We may use again our analogy of the turtle race from the bottom to the top of the hill. If we have N independent turtles, all starting from the same initial distribution, the probability distribution for the time of first passage of the top by any of them is related to the single-turtle survival probability as

$$P_{\mathrm{arr}}(N,t) = -\frac{d}{dt}S(t)^N. \tag{2}$$

If $S(t)$ were exponential for all times the distribution of first arrivals would be exponential likewise, with a maximum at $t=0$ and an average first arrival time inversely proportional to N. For very short times or very large N this clearly is unrealistic; it ignores the fact that all turtles start at the bottom of the hill and therefore will require some minimal time before they can arrive at the top at all. Obviously for short times the distribution of first arrivals has to be quite different from exponential. Van Kampen$^{(6)}$ has considered the case where the turtles start somewhere on the middle of the slope and describes the motion by a one dimensional diffusion equation of the form

$$\frac{\partial \rho(x,t)}{\partial t}=\frac{\partial}{\partial x}\left\{D\left[\frac{\partial \rho(x,t)}{\partial x}+\frac{\partial \beta\phi(x)}{\partial x}\,\rho(x,t)\right]\right\}. \tag{3}$$

Here the diffusion constant D is assumed constant[2], $\phi(x)$ describes the external potential representing the hill, and $\beta = 1/(k_B T)$, with T temperature and k_B Boltzmann's constant. Van Kampen then shows very elegantly that the distribution function for first arrival at L, starting from x, for very short times is given by

$$P_{\mathrm{sh}}(x,L,t)=\frac{L-x}{\sqrt{4\pi\, Dt^3}}\exp-\left(\frac{(L-x)^2}{4\,Dt}+\frac{\beta(\phi(L)-\phi(x))}{2}\right). \tag{4}$$

However, his result is restricted to really short times and it cannot be applied right away to the case where one starts from the origin, with a reflecting boundary imposed there.

Here I will extend his results so as to remove these limitations. The case of a strictly linear potential is solved exactly in the present section, and in the next section short time approximations are obtained for a potential hill of general shape. In Section 4 a comparison is made to numerical solutions of the diffusion equation and it is confirmed that the approximations made in Section 3 are asymptotically correct for short enough times. The average time of first arrival with N turtles starting from the origin is found to decrease as $1/\log N$ for large N.

To study the escape process in a potential $\phi(x)$ one may start by considering a continuous time random walk (CTRW) on a discrete set of points 1, 2,..., L located at positions $x_n = n\,\Delta x$, with jump rates $\Gamma_\pm(x_n)$ for jumps to the right and to the left respectively, defined through

$$\Gamma_\pm(x)=\frac{\Gamma\exp[\epsilon_\pm(x)]}{\exp[\epsilon_+(x)]+\exp[\epsilon_-(x)]}, \tag{5}$$

with

$$\epsilon_\pm(x)=\frac{-\beta(\phi(x\pm\Delta x)-\phi(x))}{2}. \tag{6}$$

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[2] If D depends on x the equation may be transformed to a diffusion equation with constant D by replacing x by y satisfying $\frac{dy}{dx}=(\frac{D}{D(x)})^{1/2}$. The potential has to be adjusted accordingly.

In a linear potential ϵ is a constant and the forward and backward jump rates Γ_+ respectively Γ_- are constants as well. As a consequence, for each CTRW realization bringing a walker in n steps from position x to L the weight equals the weight of the same realization in a symmetric CTRW with the same total jump rate Γ, times $\exp[-\beta(\phi(L)-\phi(x))/2]/\cosh^n \epsilon$. Now consider the continuum limit where $\Delta x \to 0$ and the jump frequency Γ is related to the diffusion coefficient through

$$\Gamma(\Delta x)^2/2 = D. \tag{7}$$

In this limit we may identify n with Γt, and the denominator $\cosh^n \epsilon$ becomes $\exp v_0 t$, where I introduced

$$v_0 \equiv \tfrac{1}{4}\,(\beta\phi')^2\, D. \tag{8}$$

The prime denotes the derivative with respect to x.

Consider again the probability density for first arrival at L for a diffusor starting at x, well to the right of the origin (so for short times paths involving reflection at the origin may be ignored). The method of images, combined with the observations made above, allow one to write this as

$$P_1(x, L, t) = \frac{L-x}{\sqrt{4\pi D t^3}}\, e^{-\frac{\beta(\phi(L)-\phi(x))}{2}}\, e^{-\frac{(L-x)^2}{4Dt}}\, e^{-v_0 t} \tag{9}$$

This is a well-known result, see, e.g., ref. 7. It confirms Van Kampen's short time behavior, but there is an additional damping factor which becomes important at slightly longer times.

For the linear potential the first arrival time distribution for escape at $x = L$ with a reflecting boundary at $x = 0$ has been calculated by Koplik *et al.*$^{(8)}$ A more pedagogical discussion of this calculation may be found in chapter 2 of ref. 9. Here I will use a different derivation, which is mathematically somewhat more involved, but seems more suitable for devising both simple and accurate approximations for more general potentials. For obtaining the first arrival time distribution with the boundary conditions described above we can use the following well-known observation: in general escape will take place after an arbitrary number of returns to the origin, followed by a path that does not return to the origin anymore and ends up at $x = L$. Mathematically the function describing the joint probability distribution for all these events may be obtained as the convolution of the probability density $R(t)$ of return at the origin at time t (keeping account of the discreteness of the lattice), with the probability density $P_{\rm abs}(\Delta x, L, t)$ for first arrival at L starting from site 1, with an absorbing boundary condition at the origin. The inclusion of Δx here prevents

$P_{\rm abs}(\Delta x, L, t)$ from being identically zero. Since the discreteness of the lattice also was accounted for consistently in $R(t)$, all important results will turn out independent of the precise value of Δx. Calculating the function $P_{\rm abs}(\Delta x, L, t)$ may also be done by relating the CTRW in a linear potential to the symmetric CTRW. The method of images, now applied both at $x = 0$ and $x = L$, yields

$$P_{\rm abs}(\Delta x, L, t) = 4\,\Delta x\, e^{-\frac{\beta\,\Delta\phi}{2}} e^{-\nu_0 t} \frac{\partial}{\partial t} \frac{e^{-\frac{L^2}{4\,Dt}}}{\sqrt{4\pi\,Dt}}, \tag{10}$$

with $\Delta\phi = \phi(L) - \phi(0)$. The effects of images resulting from repeated reflections were neglected, as these effects are exponentially small in the parameter $\nu_0 L^2/D$, which should be $\gg 1$.

By integrating this equation over time and using the definition of ν_0 one recovers the well-known result$^{(9)}$ that the total probability for a walk starting from $n = 1$ to escape before returning to the origin is given by

$$P^{\rm abs} = \beta\phi' e^{-\beta\,\Delta\phi}. \tag{11}$$

From this one immediately recognizes the Arrhenius behavior of $\nu_{\rm long}$, introduced in ref. 1.

For calculating the time dependent probability density for return to the origin of a walk starting at site 1 one may consider a CTRW on a semi-infinite chain in a linear potential,[3] but now with transitions from site 0 to the left forbidden (implying that the total jump rate from site 0 is reduced to Γ_+). Let $X(t)$ denote the probability density for a first return at time t to an initial site different from the origin, with the additional condition that this return is from the right. One easily shows$^{(10)}$ that its Laplace transform satisfies the equation

$$\tilde{X}(z) = \frac{\Gamma_+\Gamma_-}{(\Gamma + z)^2\,(1 - \tilde{X}(z))} \tag{12}$$

with the solution

$$\tilde{X}(z) = \frac{z + \Gamma - \sqrt{z^2 + 2\Gamma z + \Gamma^2\epsilon^2}}{2(z + \Gamma)}, \tag{13}$$

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[3] In principle one should introduce an absorbing boudary condition at $x = L$, but for short times this makes hardly any difference because the probability of absorption is minute.

where Eq. (5) was used. The Laplace transform for the distribution of return times at the origin now is obtained by summing a geometric series over n returns as

$$\tilde{R}(z) = \left[1 - \frac{1}{(z+\Gamma_+)} (z+\Gamma)\tilde{X}(z) \right]^{-1}$$

$$= \frac{z+\Gamma_+}{\frac{z}{2} + \Gamma_+ - \Gamma_- + \frac{1}{2}\sqrt{z^2 + 2\Gamma z + \epsilon^2 \Gamma^2}}. \tag{14}$$

Next, note that, for fixed D, Γ scales as $1/\epsilon^2$ as $\epsilon \to 0$. Therefore, dividing both the numerator and the denominator of the expression above by Γ, keeping the dominant terms in ϵ and using Eqs. (5), (6), and (8), we end up with

$$\tilde{R}^{\mathrm{lin}}(z) = \frac{1}{\epsilon\left(\sqrt{\frac{z}{v_{\mathrm{sh}}} + 1} - 1\right)}, \tag{15}$$

where the superscript lin was introduced to make clear that Eq. (15) denotes the solution for a linear potential. In the present case v_{sh} is identical to v_0. An inverse Laplace transform yields

$$R^{\mathrm{lin}}(t) = \frac{\beta\phi'\Gamma\,\Delta x}{4}\left(1 + \frac{e^{-v_{\mathrm{sh}}t}}{\sqrt{\pi v_{\mathrm{sh}} t}} + \mathrm{erf}\sqrt{v_{\mathrm{sh}} t}\right), \tag{16}$$

with $\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x dy \exp(-y^2)$. Now the first arrival distribution may be obtained from

$$P_{\mathrm{arr}}(t) = \int_0^t d\tau\, R(\tau)\, P_{\mathrm{abs}}(\Delta x, L, t-\tau) \tag{17}$$

For the linear potential all integrations may be done in closed form with the result$^{(11)}$

$$P_{\mathrm{arr}}(t) = e^{-\beta\,\Delta\phi}\left\{ \frac{e^{-\left(\frac{L}{\sqrt{4Dt}} - \sqrt{v_{\mathrm{sh}}t}\right)^2}}{\sqrt{\pi Dt}}\left(\beta\phi' D + \frac{L}{t}\right) + 2v_{\mathrm{sh}}\left[1 - \mathrm{erf}\left(\frac{L}{\sqrt{4Dt}} - \sqrt{v_{\mathrm{sh}}t}\right).\right]\right\} \tag{18}$$

For very short times this agrees with Van Kampen's expression, Eq. (4).

3. GENERAL POTENTIALS

For potential hills of general shape Eq. (17) of course remains valid, but we do not have explicit solutions any more. To assess the short time behavior of the first arrival distribution we need short time approximations for the return time distribution $R(t)$ and the first arrival distribution with absorbing boundary conditions $P_{\rm abs}(\varDelta x, L, t)$.

Let us restrict ourselves to cases in which the hill is high, i.e. $\beta\,\varDelta\phi \gg 1$, the bottom of the hill is at the origin and the top at $x = L$, there are no intermediate maxima and minima at almost the same height as the top or bottom, and the shape of the hill near bottom and top is smooth over length scales on which the potential variations are of order $k_B T$. Under these conditions there are three well-separated time scales. A short timescale is given by $t_{\rm sh} = L_0^2/D$, with L_0 a characteristic distance from the origin where the potential has increased by an amount of order $k_B T$. On this time scale an initial distribution localized near the origin approaches an equilibrium-like distribution over a potential range of a few $k_B T$ around the origin. This is the range within which the major part of all turtles will be found at any time. An intermediate time $t_{\rm med}$, is set by the average time a turtle needs to get from bottom to top, in case it does not return to the bottom. This is the time scale required to establish the full metastable distribution. The longest time scale is $t_{\rm esc} = \nu_{\rm esc}^{-1}$, the average escape time or arrival time. For the linear potential one may choose

$$\begin{aligned} t_{\rm sh} &= (4\nu_0)^{-1} = 1/((\beta\phi')^2\, D) = L^2/((\beta\,\varDelta\phi)^2\, D), \\ t_{\rm med} &= L^2/(\beta\,\varDelta\phi\, D), \\ t_{\rm esc} &= t_{\rm sh}\, \exp(\beta\,\varDelta\phi). \end{aligned} \tag{19}$$

Under the given assumptions indeed all three scales are well separated, though the separation between $t_{\rm sh}$ and $t_{\rm med}$ is much smaller than that between $t_{\rm med}$ and $t_{\rm esc}$.

Now one may formulate short time approximations for more general hill shapes. Assign to each random walk realization the Hamiltonian

$$H(\{x_i\}) = \sum_i \left\{ \frac{\phi(x_{i+1}) - \phi(x_i)}{2} + \frac{1}{\beta} \log\left(\frac{\exp[\epsilon_+(x_i)] + \exp[\epsilon_-(x_i)]}{2} \right) \right\}, \tag{20}$$

with i running over all steps of the walk and x_i the position before the $i+1$th step. The probability for moving from x_0 to x_t in a time t under specific boundary conditions BC then may be obtained as

$$P(x_0, x_t \,|\, \mathrm{BC}) = \langle e^{-\beta H} \rangle_{x_0, x_t, \mathrm{BC}}\, P_0(x_0, x_t \,|\, \mathrm{BC}), \tag{21}$$

with $P_0(x_0, x_t \,|\, \mathrm{BC})$ the corresponding probability for the unbiased random walk. The average $\langle\,\rangle$ runs over all unbiased continuous time random walks, properly weighted, starting at x_0, ending at x_t and satisfying the required boundary conditions. For short times this average may be replaced by the Rosenstock approximation$^{(12)}$

$$P(x_0, x_t \mid \mathrm{BC}) = e^{-\beta\langle H\rangle_{x_0, x_t, \mathrm{BC}}} P_0(x_0, x_t \mid \mathrm{BC}). \tag{22}$$

In the continuum limit this reduces to

$$P(x_0, x_t \mid \mathrm{BC}) = \exp - \frac{\beta(\phi(x_t) - \phi(x_0)) + \langle(\beta\phi')^2/2 + \beta\phi''\rangle\, Dt}{2} P_0(x_0, x_t \mid \mathrm{BC}), \tag{23}$$

where the subscripts on the random walk average were omitted. Equation (23) is especially useful as an approximation for $P_{\mathrm{abs}}(\Delta x, L, t)$. For short times, unbiased walks from Δx to L with absorbing boundary conditions at the origin and at $x = L$, on average spend equal time in equal intervals, except for very small neighborhoods of the end points. There the average time spent is smaller due to the absorbing boundaries. Therefore the average $\langle\frac{(\beta\phi')^2}{4} + \frac{\beta\phi''}{2}\rangle$ may be replaced by a spatial average over the interval $(0, L)$ and one obtains the approximation

$$P_{\mathrm{abs}}^{\mathrm{sh}}(\Delta x, L, t) = 4\, \Delta x\, e^{-\frac{\beta\,\Delta\phi}{2}} e^{-\nu_{\mathrm{abs}} t} \frac{\partial}{\partial t} \frac{e^{-\frac{L^2}{4\,Dt}}}{\sqrt{4\pi\, Dt}}, \tag{24}$$

with ν_{abs} the spatial average of $(\frac{(\beta\phi')^2}{4} + \frac{\beta\phi''}{2})\, D$.

For the return probability to the origin the approximation (23) in principle could be used as well, but in this case it gives rise to somewhat cumbersome integrals involving error functions. And in fact we don't really need this: for short times in typical cases the diffusion effectively takes place near the origin in either a linear or a quadratic potential, so one may approximate the return probability by the explicit expressions for these potentials. In the case of a linear potential this becomes Eq. (16), with

$$\nu_{\mathrm{sh}} = \frac{(\beta\phi'(0))^2}{4}, \tag{25}$$

and ϕ' replaced by $\phi'(0)$ likewise. For potentials that are quadratic near the origin the return probability may be obtained from the Green function $G(x, x_0, t)$ for diffusion in a quadratic well$^{(13)}$ as

$$\begin{aligned} R^{\mathrm{qu}}(t) &= \Gamma\, \Delta x\, G(0, 0, t) \\ &= \frac{\Gamma\, \Delta x\, \kappa(0)}{2\sqrt{(1 - \exp[-2\beta\phi''(0)\, Dt])}}, \end{aligned} \tag{26}$$

with $\kappa(x)$ defined as[4] $\kappa(x)=\sqrt{(2\beta\,|\phi''(x)|)/\pi}$. In either case the short time behavior of the arrival time distribution is obtained according to Eq. (17) as the convolution of the return probability with the arrival probability with absorbing boundary conditions. For times $\ll t_{\mathrm{sh}}$ the exponential damping factors $\exp-\nu_{\mathrm{sh}}t$ and $\exp-\nu_{\mathrm{abs}}t$ may be ignored and one finds that the arrival probability asymptotically is given by the Van Kampen expression,$^{(4)}$ so

$$P^{\mathrm{sh}}_{\mathrm{arr}}(t)=\frac{Le^{-\frac{\beta\,\Delta\phi}{2}}e^{-\frac{L^2}{4Dt}}}{\sqrt{\pi\,Dt^3}},\tag{27}$$

irrespective of the shape of the potential.

To find the average first arrival time for very large numbers of turtles, notice that for times $\ll t_0$ the survival probability for a single turtle may be obtained from Eqs. (17), (24), and (27) as

$$S(t)=1-\int_0^t d\tau\, P^{\mathrm{sh}}_{\mathrm{arr}}(t)\approx 1-4\sqrt{\frac{Dt}{\pi L^2}}\,e^{-\frac{\beta\,\Delta\phi}{2}}e^{-\frac{L^2}{4Dt}}.\tag{28}$$

The mean first arrival time for the case of N turtles may be found by setting the term subtracted from unity equal to $1/N$; for this time the probability that no turtles have arrived yet equals $(1-1/N)^N\sim 1/e$, whereas for only slightly shorter times this probability still is almost unity and for only slightly longer times it has almost decayed to zero. This leads to

$$\bar{t}_{\mathrm{esc}}(N)=\frac{L^2}{4D\left(\log N-\frac{\beta\,\Delta\phi}{2}-\log\left(\frac{L}{4}\sqrt{\frac{\pi}{D\bar{t}_{\mathrm{esc}}(N)}}\right)\right)}.\tag{29}$$

From this one rapidly sees that for $N\gg\exp(\beta\,\Delta\phi/2)$ the first arrival time approaches zero as $1/\log N$. This is much slower indeed than the $1/N$ behavior one would find for smaller values of N, such that typically a quasi-stationary distribution over the full slope is reached well before the first turtle escapes.

Equations (2), (27), and (28) may also be used to consider fluctuations in $t_{\mathrm{esc}}(N)$. One readily finds that

$$\left(\frac{t_{\mathrm{esc}}(N)-\bar{t}_{\mathrm{esc}}(N)}{\bar{t}_{\mathrm{esc}}(N)}\right)^2\sim\frac{1}{\log^2 N}.\tag{30}$$

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[4] This may be generalized to the case of a potential of form $\phi(x)=\phi(0)+cx^\alpha$, respectively $\phi(x)=\phi(L)-c(L-x)^\alpha$. In this case one obtains $\kappa=(\beta c)^{-1/\alpha}\,\Gamma(\frac{\alpha+1}{\alpha})$.

So the distribution of $t_{\mathrm{esc}}(N)$ becomes sharp for very large N. This is in marked contrast to the case of a Poisson distribution, where relative fluctuations are independent of N.

4. NUMERICAL RESULTS

Numerical results were obtained by solving discrete time random walks on a lattice of L sites, in a number of different potentials. At each time step a fixed fraction Γ of the walkers are moved to their neighboring sites, with jump probabilities satisfying Eq. (5). Walkers reaching the top of the hill are taken out of the system. This is done most efficiently in an exact enumeration scheme, where one starts from an initial density distribution, typically concentrated at the origin, and evolves this distribution in discrete time in accordance with the jump probabilities. In this way it is possible to capture also the very small arrival probabilities at short times.

In all the calculations reported here $L = 10{,}000$, $\Gamma = 0.04$ and the potential difference between bottom and top of the hill is $\Delta\phi = 20k_BT$. Besides the linear potential I considered four different potentials with all possible combinations of zero and non-zero slope at $x = 0$ respectively $x = L$. Specifically, these potentials were of the forms

$$\phi(x) = \Delta\phi \frac{x}{L} \qquad \text{linear,}$$

$$\phi(x) = \Delta\phi \left(\frac{x}{L}\right)^2 \qquad \text{quadratic,}$$

$$\phi(x) = \Delta\phi \left(\frac{2x}{L} - \left(\frac{x}{L}\right)^2\right) \qquad \text{inverse quadratic,}$$

$$\phi(x) = \Delta\phi \left(4\left(\frac{x}{L} - \frac{1}{2}\right)^3 + \frac{1}{2}\right) \qquad \text{cubic,}$$

$$\phi(x) = \frac{1}{2}\Delta\phi \left(1 - \cos\frac{\pi x}{L}\right) \qquad \text{cosine.}$$

The cubic potential, besides having non-zero slopes at the end also goes through a point of zero slope in the middle. Altogether this choice of potentials provides a check on the accuracy of the short-time approximations developed in the preceding section, under a large variety of conditions. Figure 1 shows a comparison of the first arrival probabilities resulting from the exact enumeration scheme to the predictions of Eq. (17), combined with (24) and (16) or (26). The linear potential, for which we

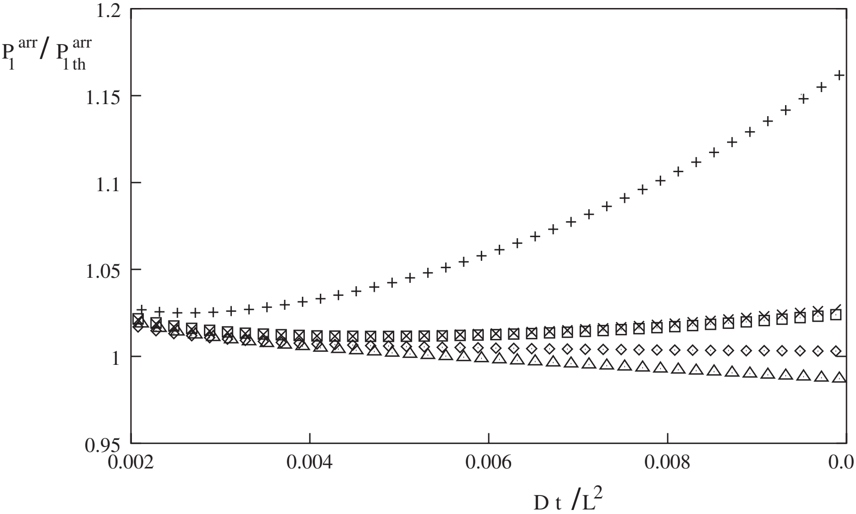

Fig. 1. The time dependence of the arrival probability is compared to the theoretical predictions for short times. For five different shapes of the potential hill the ratio of the numerical solution of the diffusion equation to the theoretical expression is plotted as function of Dt/L^2. The exact enumeration results for the linear potential (diamonds) are compared to the exact solution, Eq. (18) and those for the quadratic (crosses), the inverse qudratic (squares), the cubic (pluses) and the cosine (triangles) potential to the numerical solution of Eqs. (17) together with (24) and (16) or (26).

have the exact result (18), provides a check on the accuracy of the discretized dynamics as an approximation for the diffusion equation.[5] Figure 1 shows for the linear potential the ratio of the exact enumeration results to those of Eq. (18), as function of the dimensionless time $\tau \equiv \Gamma n/2L^2$, with n the discrete time in the enumeration scheme. On this scale the relaxation time ν_{sh}^{-1} corresponds to $\tau = 0.01$. One sees that the discretization effects remain limited to less than 2.5%, on the shortest time scales yielding an arrival probability different from zero within the computer accuracy. They decay to less than 1% for larger τ. Instead of Eq. (18) one may also use (17), combined with (24) and (16). This everywhere yields slightly larger values, but the difference never exceeds 0.4%. For all the other potentials the results for times up to t_{br}, with $t_{br} = \min(\nu_{sh}^{-1}, \nu_{abs}^{-1})$, remain within a deviation of 3% of the analytic approximation. The largest deviations over the full time ranged considered occur for the cubic potential,

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[5] Here one should keep in mind that in actual applications often the diffusion equation is obtained as a continuum approximation for dynamics that are in reality discrete in the spatial coordinates.

which indeed of all potentials considered has the shortest t_{br} (namely $t_{\mathrm{br}} = 0.0011\cdots$). Part of the deviations always are due to discretization errors, as seen already for the linear potential. But given that the numbers divided upon each other to obtain these curves, easily vary over more than a hundred orders of magnitude within the time range considered, errors of a few percent may be considered quite a good result. It should be noted that, in order to have this good agreement over the time range considered, inclusion of the damping term $\exp(-\nu_{\mathrm{abs}} t)$ in ref. 24, with the value of ν_{abs} as specified below this equation, is crucial.

5. DISCUSSION

In this paper I obtained the short time behavior of the first arrival probability at the top of a potential hill for a diffusion process or random walk starting at the bottom. It is strongly suppressed during an initial time interval on the order of the diffusion time from bottom to top in the absence of a potential. In the continuum diffusion description it never becomes strictly zero for positive times, but it approaches zero extremely rapidly as time goes to zero. The arrival probability for very short times becomes fully independent of the shape of the potential, but the time range over which this holds becomes shorter as the potential gets higher and steeper near the origin.

For slightly longer times the inclusion of exponential damping factors in the expressions for the first arrival probability does become important. E.g. ignoring the second derivative term in the expression for ν_{abs} below Eq. (24) leads to a deviation of roughly 20% at $\tau = 0.01$ for the quadratic and the inverse quadratic potential, whereas the deviations with the full expression are only about 1%.

It is obvious that the delay time t_D introduced in Eq. (1) has to be of the order t_{med}, so the factor $\exp(\nu_{\mathrm{long}} t_D)$ is very close to unity. Explicit expressions for t_D may be obtained from the projection of the initial distribution on the most slowly decaying eigenfunction of the diffusion equation (3) with escape at $x = L$. Most notable is that t_D in essence is independent of the precise form of the initial distribution, as long as this remains localized within a region of width L_0 around the origin, where the value of the potential remains less than a few $k_B T$ above that in the origin.

The average first arrival time for a very large number of independent random walkers, all starting at or near the bottom, does not scale as the inverse of the number of walkers N, as one might expect on the basis of Poisson statistics, but rather as $1/\log N$. This may have important consequences in large metastable systems, in which the first nucleation of a stable droplet has an immediate large effect on the whole system.

It is an interesting question how accurately such systems may be described by a simple model of noninteracting random walks in one dimension. A priori it is not clear that the nucleating droplets are characterized sufficiently by a single parameter giving their size, ignoring all details about their shapes. Interactions between droplets may play a role, especially when their density becomes larger. And, especially in the presence of conservation laws there may be memory effects that make a simple random walk picture inadequate. Presently these questions are under investigation both numerically and analytically and we expect to report on them soon.(14)

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With great pleasure I dedicate this paper to Michael Fisher, who has been an enlightening guide showing us new ways to go for so many decades now. I wish him an equally good continuation of his activities after his seventieth birthday. I thank Gerard Barkema and Reinier Bikker for very helpful discussions and assistance with computer manipulations. Support by the Statistical physics program of FOM is gratefully acknowledged.

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