Role of Ito's lemma in sampling pinned diffusion paths in the continuous-time limit

P. J. Malsom and F. J. Pinski*
Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221, USA
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We consider pinned diffusion paths that are explored by a particle moving via a conservative force while being in thermal equilibrium with its surroundings. To probe rare transitions, we use the Onsager-Machlup (OM) functional as a path probability distribution function for transition paths that are constrained to start and stop at predesignated points in different energy basins after a fixed time. The OM theory is based on a discrete-time version of Brownian dynamics, and thus it possesses a finite number of time steps. Here we explore the continuous-time limit where the number of time steps, and hence the dimensionality, becomes infinite. In this regime, the OM functional has been commonly regularized by using the Ito-Girsanov change of measure. This regularized form can then be used as a basis of a numerical algorithm to probe transition paths. In doing so, time again is discretized, progressing in fixed increments. When sampling paths, we find that numerical schemes based on this regularized continuous-time limit can fail catastrophically in describing the path of a particle moving in a potential with multiple wells. The origin of this behavior is traced to numerical instabilities in the discrete version of the continuous-time path measure that are not present in the infinite-dimensional limit. These instabilities arise because of the difficulty of satisfying, in finite dimensions, the conditions imposed by Ito's lemma that was an essential ingredient in the derivation of the regularized continuous-time measure. As an important consequence of this analysis, we conclude that the most probable diffusion path is not a physical entity because the thermodynamic action is effectively flat and cannot be minimized.

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I. INTRODUCTION

Much of the current work in the study of diffusion processes is grounded in an expression for the probability of a succession of states of a spontaneously fluctuating thermodynamic system [1–5]. This expression, famously reported in the 1953 article of Onsager and Machlup [6], has become known as the Onsager-Machlup (OM) functional. As in the original 1953 article, we represent the fluctuations by white noise, spatially and temporally uncorrelated, and whose amplitude is given by the fluctuation-dissipation theorem. The underlying motion is then expressed in terms of Brownian dynamics. Here we explore an extension of these works, which leverages the continuous-time limit of the OM functional [7] to sample *paths* and show that numerical algorithms based on this commonly used approach possess instabilities that render the algorithms unreliable.

The OM functional can be used to study rare events [1,8–10]. But what does one mean by "rare"? For the purposes of this paper, we divide rare events into two groups: those consistent with thermodynamics and those that are not. As an example of the latter, what we call *extremely* rare events, consider the very small probability that all the molecules in a room might migrate to one corner. Even though this is allowed by statistical mechanics, if we observed such an event, we would have witnessed a violation of thermodynamics. We are not, nor were Onsager and Machlup [6], interested in these *extremely* rare events. We are interested in rare events that are consistent with thermodynamics, ones that are driven by the fluctuations inherent in a thermodynamic system.

In the 1970s, the original OM functional was extended to the continuous-time limit using Girsanov theorem to express the Radon-Nikodym derivative. And with the assistance of Ito's lemma, the stochastic integration was eliminated. This continuous-time probability measure, which we will refer to as the Ito-Girsanov measure, generated considerable attention [11–24]. This limiting procedure has been accepted as a method that can be used to look at rare events by constructing probabilities for pinned diffusion paths [9,13,25–29]. An extension of this limiting procedure, proposed by Graham [13], and later Eyink [30], stressed the generalization of a "least-action" principle to describe particle motions, which then led to the notion of the thermodynamic action.

In this paper, we concentrate on the use of this Ito-Girsanov continuous-time limit of the OM function in path-sampling schemes. In particular, we show that such numerical implementations suffer from catastrophic instabilities. Furthermore, we show that there is no "action" to minimize: the path probabilities are independent of the details of the particle motions as these probabilities are a result of the noise that originates in the thermal bath. This statement may come as a bit of a surprise since the maximizer of Ito-Girsanov probability provides the center of a ball of maximum probability of the limiting OM functional; see Dürr and Bach [12]. Remember that in the derivation of the Ito-Girsanov measure, one uses a substitution justified by Ito's lemma. Underlying Ito's lemma is a hidden assumption that in the diffusion path, the noise history and the path positions are not correlated with one another. Any structure in the maximizers of the Ito-Girsanov measure are washed out and canceled by the "entropic" effect of the multiplicity of paths in infinite dimensions that are inherent in the continuous-time limit. Since computer algorithms must have a finite representation, they do not contain this infinite multiplicity and thus they do not give the correct weight to this entropic effect. Consider an analogy to an example in equilibrium thermodynamics. There, energy minima exist but entropy plays an important role, as the free-energy minimum

*frank.pinski@uc.edu

gives the physical state. As one takes the continuous-time limit, the number of dimensions, the number of degrees of freedom, grows because in Brownian dynamics, the paths are rough with structure even at the tiniest of timescales. In the limiting process, the entropic effects arising from the growing number of degrees of freedom nullify the importance of this ball. As we see below, in the continuous-time limit, any variation in the Ito-Girsanov expression is immaterial compared to the effect of the path multiplicity. Thus the most probable path (MPP) is not a physical entity for a particle being buffeted by spontaneously fluctuating Brownian forces.

The organization of this paper is as follows. We begin presenting details of the system dynamics and present the mathematical framework that we are studying. After establishing the groundwork, we closely examine the idea that the path probability distribution is effectively flat, and thus there is not a "thermodynamic action" to minimize. We show that unphysical paths are produced by numerical simulations that are based on the Ito-Girsanov measure. We then closely examine the numerics and expose the origins of the unphysical nature of the paths. Finally, we summarize and end with a discussion of the impact of the results reported here.

II. BROWNIAN DYNAMICS AND THE CONTINUOUS-TIME PATH PROBABILITY

Throughout this paper, we will consider a particle in contact with a heat reservoir at a temperature ϵ. It is moving under the influence of a potential $\mathbb{V}(x)$ with the deterministic force being $F(x) = -\mathbb{V}'(x)$. Note that although the equations are written for the one-dimensional case for clarity, the formalism can easily be extended to higher dimensions and for a collection of particles.

The main focus of this paper is on methods for sampling paths of particles that are moving according to Brownian dynamics. The underlying equation of motion is given by the stochastic differential equation (SDE):

$$dx = F(x_t)\,dt + \sqrt{2\epsilon}\,dW_t, \tag{1}$$

where dW_t is the standard Wiener process that represents the (uncorrelated) Gaussian noise. Using a discrete time step, Δt, one typically uses the Euler-Maruyama algorithm [31] as an approximate method for propagating the position as a function of time. In particular,

$$x_{i+1} = x_i + F(x_i)\,\Delta t + \sqrt{2\epsilon\,\Delta t}\;\xi_i, \tag{2}$$

where ξ_i is a Gaussian random variate with mean zero and unit variance. Successive applications (N times) of this equation produces a sequence of positions $\{x_i\}$, which is called a path. Onsager and Machlup [6] used the underlying thermal fluctuations to write the path probability in terms of the path variables themselves, namely,

$$-\ln \mathbb{P}_p = \mathbb{C} + \frac{\Delta t}{2\epsilon}\sum_{i=1}^{N}\frac{1}{2}\left[\frac{x_{i+1}-x_i}{\Delta t} - F(x_i)\right]^2, \tag{3}$$

where $\mathbb{C}$ is a constant that is unimportant for this paper. This equation defines what is sometimes called the thermodynamic action and other times, the OM functional. At this point, it is important to emphasize that the path probability, $\mathbb{P}_p \propto \Pi_i \exp(-\frac{1}{2}\xi_i^2)$, is generated from a large set of Gaussian variates whose origins rest in the thermal reservoir and are independent of the system under study. If one labels each set and then plots $\mathbb{P}_p$ as a function of this index, one would find that the path probability is almost constant. In the absence of forces, this is intuitively obvious: for free Brownian motion, no path is more probable than any other (paths of the same duration). When a force is present, the expression for the path probability, $\mathbb{P}_p \propto \Pi_i \exp(-\frac{1}{2}\xi_i^2)$, is unchanged. Thus, even for diffusions with nonzero forces, all paths of the same duration are equally probable. Any outliers are the extremely rare events that are not thermodynamically significant.

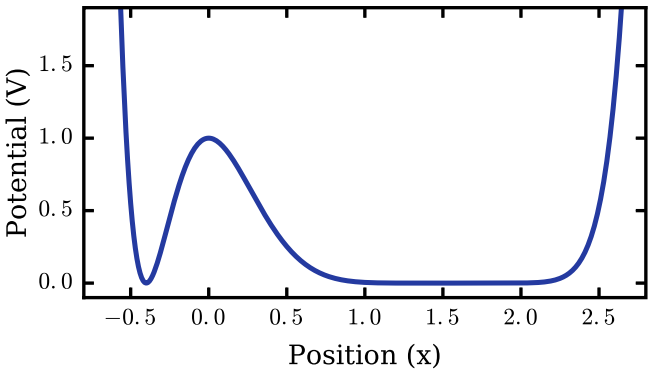

FIG. 1. A plot of the double-well potential used in this paper [see Eq. (6)]. A narrow (quadratic) well, on the left, is separated from the broad well on the right by a unit energy barrier.

In the continuous-time limit, the path probability diverges, as it can be informally written as $\overline{\mathbb{P}}_p \propto \exp(-\frac{1}{2}\int_0^T dt\,|\frac{dW}{dt}|^2)$. In this limit, using Ito calculus and the Girsanov theorem, the Radon-Nikodym derivative is used to express the change in the measure [7] as

$$\frac{d\overline{\mathbb{P}}_p}{d\mathbb{Q}_p} = \exp\left[-\frac{1}{4\epsilon}\int_0^T dt\,|F(x_t)|^2 + \frac{1}{2\epsilon}\int_{x_0}^{x_T} dx_t\,F(x_t)\right], \tag{4}$$

where T is the duration of the path, $\overline{\mathbb{P}}_p$ is the continuous-time limit of $\mathbb{P}_p$, $\mathbb{Q}_p$ is the measure associated with free Brownian motion, and the path starts at x_0 and ends at x_T. One can eliminate the stochastic integral [the last term in Eq. (4)] by using Ito's lemma. The Ito-Girsanov change of measure is defined to be

$$\frac{d\overline{\mathbb{P}}_p}{d\mathbb{Q}_p} = \exp\left\{-\frac{1}{2\epsilon}\left[\mathbb{V}(x_T) - \mathbb{V}(x_0) + \int_0^T dt\;G(x_t)\right]\right\}, \tag{5}$$

where the function $G(x)$ is defined as $G(x) = \frac{1}{2}|F(x)|^2 - \epsilon\,\mathbb{V}''(x)$. It is this equation [Eq. (5)] that we use as the basis of numerical algorithms for sampling paths in the continuous-time limit.

We have constructed a one-dimensional potential to highlight one of the key components of the measure. Looking at Eq. (5), the Ito-Girsanov expression seems to favor regions where the curvature of the potential is the greatest, independent of the value of the potential itself. For this reason we consider the potential (see Fig. 1)

$$\mathbb{V}(x) = 2^{-26}(8-5x)^8\,(2+5x)^2, \tag{6}$$

which has two degenerate wells with a barrier of unity at the origin. A narrow (quadratic) well is on the left and a wide well is on the right. By making the wells degenerate, we eliminate the large (exponential) dependence due to energy differences, and we accentuate the curvature effects by making one well much wider than the other.

III. EQUIVALENCE OF PATH PROBABILITY

We now turn to a general discussion of the idea of a most probable path (MPP) in the OM formalism by examining the relative probability of paths. As in any continuous distribution, while the probability of any one path is zero, the relative probability of two paths is well-defined. First consider paths generated by free Brownian motion, where the potential acting on the system is zero. All paths of a fixed length in this free case will have equal probability (relative to one another), except for extremely rare instances that are not thermodynamically significant. The path probability $\mathbb{P}_p$ is governed by the underlying Gaussian noise, $\mathbb{P}_p \propto \Pi_i \exp(-\frac{1}{2}\xi_i^2)$, where the set $\{\xi_i\}$ is independent of the position of the particle. For free Brownian motion, it is easy to accept that, for finite representations, the expression for $\mathbb{P}_p$, is the same value for all paths. This result holds for paths of fixed length as the size of the time increment becomes infinitesimally small and is put on a more formal basis by invoking large deviation results [32]. Furthermore, when one adds a deterministic force, the expression for the path probability $\mathbb{P}_p$ is unchanged, and leads to the conclusion that all paths of the same length are equally probable. The physical interpretation of this statement is that the noise originates in the heat bath [33] and has no knowledge of the underlying forces inherent in the system.

To illustrate the above point, consider the following "thought" experiment. For a conservative force, consider sampling the Boltzmann distribution using the Brownian dynamics as expressed by Eq. (2). Take the starting point, x_0, to be arbitrary and integrate the SDE over a fixed time, T, that is long compared to any barrier hopping time. Using a nonzero but small time step, Δt, one uses $N_r = T/\Delta t$ Gaussian random variates. Keeping the same set of random numbers, but simply permuting the order, redo the integration. This procedure provides $N_r!$ possible paths, each with identical probabilities. For large enough T and small enough Δt, the set of endpoints, x_T, should be distributed in a manner that is close to Boltzmann. Here it is important to recognize that it is not the path probability that creates the distribution, as all paths are identically probable. Rather it is the path density that drives the correct distribution of the endpoints. Positions along a long path reflect the thermodynamic Boltzmann distribution. Thus, when one generates an ensemble of such paths, the endpoints must also reflect the Boltzmann distribution. A large number of paths of the ensemble will end near the potential minimum; a smaller number near the maximum.

We have partially performed this numerical experiment (calculation) for the potential defined in Eq. (6). We chose $N_r = 2 \times 10^6$ random numbers, Gaussian distributed with mean zero and variance one. Out of the possible $N_r!$ paths we followed over 400 000 of them using the Euler-Maruyama algorithm, with $\Delta t = 0.0005$. The endpoints were then collected and their histogram is displayed in Fig. 2. Evidently the distribution looks to be very close to the Boltzmann distribution in spite of the fact that each path has the identically equivalent path probability. Similar results are expected when one generates independent sets of random numbers instead of using the permutations of the original set.

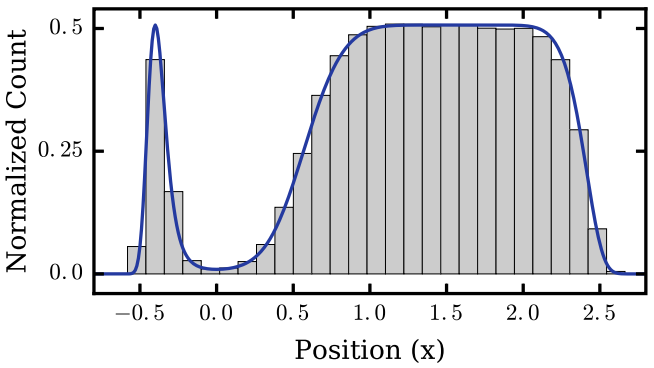

FIG. 2. The histogram of endpoints of the set of trajectories with equal probability. Here the endpoints of 472 640 different trajectories are shown. The solid curve is the normalized Boltzmann distribution, $\exp(-\mathbb{V}/\epsilon)/Z$, for the temperature $\epsilon = 0.25$, and potential given by Eq. (6).

The noise is a consequence of the random fluctuations of the thermal reservoir, and in the SDE given in Eq. (1), the noise is not correlated with the position of the particle. By inspecting Eq. (5), we see that it gives different probabilities for different paths: some paths are more probable than others. This is accomplished by correlating the noise with the positions through the function G. It is clearly incorrect to interpret the Ito-Girsanov expression in this manner.

IV. AWAY FROM THE CONTINUOUS-TIME LIMIT

One of the uses of the OM functional is to incorporate it into a scheme to sample paths that are constrained at both ends. The aim is to efficiently generate an ensemble of paths that include a transition over an energy barrier. When the barrier is large compared to the typical thermal energy, the transition is a rare event. We wish to explore barrier hopping that is consistent with thermodynamics, where the driving noise reflects the fluctuating random effects that originate in a thermal bath and thus are independent of the particle's position.

The quandary is that for a very simple one-dimensional example, the generated paths quickly become unphysical when using the Ito-Girsanov form, $\overline{\mathbb{P}}_p$, for the path probability. Long paths, generated with small time steps, are expected to be consistent with equilibrium thermodynamics. First we address the question of what happens away from the continuous-time limit and show that it is possible to use an algorithm that generates a collection of paths that are consistent with the Boltzmann distribution. Then we show that when we use Ito-Girsanov expression, given by Eq. (5), we obtain results that are unphysical.

To understand how the time discretization affects the numerical solution to the SDE we used both Eq. (3) and the

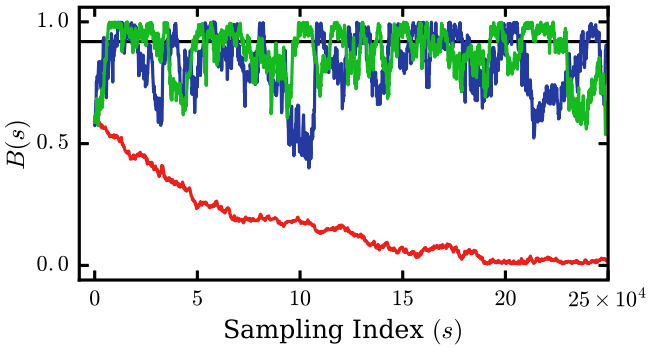

FIG. 3. The fraction of the path in the broad well, $B(s)$, is shown as a function of the sampling index, s. These are results for three calculations. We started with the same input path where $B(0) \approx 0.6$, and had a path length of $T = N\,\Delta t = 150$, and a time step along the path of $\Delta t = 0.005$. The lower (red) curve corresponds to the results using the Ito-Girsanov expression. While the upper curves, green (light gray) and blue (dark gray), are the results of using the functionals [Eqs. (3) and (7)], which are based on a discrete time grid. The straight line (at 0.92) corresponds to the equilibrium value.

following form of the path probability $\mathbb{P}^s_p$:

$$-\ln \mathbb{P}^s_p = \mathbb{C} + \frac{\Delta t}{2\epsilon}\sum_{i=1}^{N}\left(\frac{1}{2}\left|\frac{x_{i+1}-x_i}{\Delta t} - F(\overline{x}_i)\right|^2 - J_i\right), \tag{7}$$

where $J_i = \frac{2\epsilon}{\Delta t}\ln[1 - \frac{\Delta t}{2}F'(\overline{x}_i)]$, and $\overline{x}_i$ is the midpoint of x_i and x_{i+1}. This expression, $\mathbb{P}^s_p$, is related to the Stratonovich representation of the diffusion process (see Elber and Shalloway [34]). As indicated by Van Kampen [35], for the problem described by Eq. (1), the limits of both the Ito and Stratonovich discretizations are equivalent. However, as Lavenda [20] pointed out, Eq. (7) must differ from Eq. (3) since the Jacobian term J_i strays from unity. In the continuous-time limit $J_i \Rightarrow \epsilon\, F'(\overline{x}_i)$, which provides the Laplacian term in the definition of G, giving the same limit as seen in the Ito-Girsanov expression in Eq. (5).

In sampling $\mathbb{P}_p$ and $\mathbb{P}^s_p$, we generated a sequence of paths at a temperature $\epsilon = 0.25$, constrained to start in the narrow well and to end in the broad well and used a HMC implementation [36] using the "Implicit Algorithm" in Beskos *et al.* [37]. We use the Heaviside function Θ to define the function $B(s)$ to be the fraction of the path that is contained in the broad well, namely,

$$B(s) = \frac{1}{T}\int_0^T dt\ \Theta\big(x_t^{(s)}\big) \approx \frac{1}{N}\sum_i \Theta\big(x_i^{(s)}\big),$$

where the sampling index is denoted as s, and the corresponding path is $\{x_i^{(s)}\}$.

As can be seen in Fig. 3, using either of the path probabilities given by a discrete sum, we find an ensemble of paths that are concentrated in the wide well. All paths are constrained to undergo at least one transition; we find only one transition in the majority of paths, and a smaller number of paths that undergo multiple transitions. Using either expression, the percentage of the time spent in the broad well is, on average, approximately 85%, which is much closer to the equilibrium value of 90%. This is the type of behavior that one expects for paths consistent with the Boltzmann distribution. Away from the continuous-time limit, we found a behavior that is close to the physical result. In the next section, we show that these are in stark contrast to calculations that sample the path probability expression given by the Ito-Girsanov expression [Eq. (5)].

V. UNPHYSICAL RESULTS

Now we turn to the results found when sampling from the path probability given by the Ito-Girsanov expression, $\overline{\mathbb{P}}_p$ [Eq. (5)]. Results generated using the Ito-Girsanov expression have been questioned before. For example, in Adib's paper [38], the origins of the poor performance when using the Ito-Girsanov expression were not understood. The potential used in this work [Eq. (6)], was designed to highlight effects on transition paths of the potential-curvature terms in the Ito-Girsanov expression. With degenerate wells, these curvature terms enhance the time the particle will spend in the narrow well. From the form of $\overline{\mathbb{P}}_p$, the curvature of the narrow basin would seem to enhance the probability of paths that spend a long time there; see the early paper of Weiss and Häffner [23]. Indeed, the MPP [39] would be highly concentrated in the narrow well.

We used the Ito-Girsanov formula with the method developed by Beskos *et al.* [40], referred to here as the path-space hybrid Monte Carlo (psHMC), using a temperature $\epsilon = 0.25$, to generate a sequence of paths constrained to start in the narrow well and to end in the broad well. In Fig. 3, we plot $B(s)$ using the described procedure (red curve), showing that the paths quickly become unphysical in that the particle spends the vast majority of the time in the narrow well. Such paths are inconsistent with the equilibrium thermodynamical distribution where the particle would be expected to be found in the broad well about 90% of the time. Although only one sampling set is presented here, we note that this effect is robust in that similar results are obtained for a range of parameters.

VI. NUMERICAL ASPECTS

To summarize the previous section; we found that the discrete version and the continuous-time limit of the OM functional generate opposing behavior when sampling pinned paths for a particle moving in a simple double-well potential. We generated an ensemble of paths that were consistent with the Boltzmann distribution by using discrete forms of the OM functional with an HMC algorithm with an Ito discretization or with a Stratonovich discretization, away from the continuous-time limit. Conversely, we generated an ensemble of paths that were concentrated in the narrow well using the Ito-Girsanov expression using the psHMC algorithm.

The key to understanding numerics behind these results is to examine the "cross term" in Eq. (3). Using the Taylor expansion of $\mathbb{V}(x_{i+1})$, the cross term can be written as

$$(x_{i+1}-x_i)F(x_i) = \mathbb{V}(x_{i+1}) - \mathbb{V}(x_i) + \epsilon\,\Delta t\, F'(x_i) + \overline{\Delta}_i, \tag{8}$$

where to second order in Δx, the expression for $\overline{\Delta}_i$ is

$$\overline{\Delta}_i \approx \left(\tfrac{1}{2}(x_{i+1}-x_i)^2 - \epsilon\,\Delta t\right) F'(x_i). \tag{9}$$

If one ignores $\overline{\Delta}_i$, Eq. (8) is a discrete form of Ito's lemma. The first term on the right-hand side of Eq. (8) gives the change-in-potential term in Eq. (5) (as it telescopes under summation), while the second term gives the Laplacian term in the Ito-Girsanov expression. Examining $\sum_i \overline{\Delta}_i$, we see that it is small only when the noise, embodied by Δx^2 and the position are not correlated, or when F' is a constant. Remember that the noise and positions being uncorrelated is a consequence of the original SDE [Eq. (1)], and therefore it is a requirement for generating thermodynamically consistent paths. Over short timescales, due to the rapid variation in the noise term, the high-frequency contributions can be ignored [41]. But this is not sufficient; the small-frequency contributions must also be negligible.

Away from the continuous-time limit, one uses Eq. (3) or Eq. (7) which can be considered as discrete versions of Eq. (4). The quadratic form of these measures ensure that $\sum_i \overline{\Delta}_i$ remains small. However, for a nonvanishing value of the time step, Δt, nothing in the Ito-Girsanov expression, Eq. (5), constrains $\sum_i \overline{\Delta}_i$ and the sum is free to grow to maximize the Ito-Girsanov expression. As discussed above, in the continuous-time limit, the variation in the Ito-Girsanov expression is not relevant, as the path multiplicity swamps any such variation.

As shown above, by numerically sampling this measure, we observe large values of $\sum_i \overline{\Delta}_i$ when using the psHMC algorithm. In the psHMC algorithm the implied noise history and the particle position are intertwined as one searches for the paths that have the larger probabilities as indicated by the Ito-Girsanov expression. During the search, correlations are introduced into the low end of the frequency spectrum while the path evolves under the (deterministic) Hamiltonian flow. The implication of such low-frequency correlation is that the thermal bath is no longer independent of the system and thus the fluctuations are no longer thermodynamic, and entropy is spuriously generated [42]. Remember that this behavior is a consequence of not having properly included the effect of the infinite number of degrees of freedom. In finite-dimensional implementations of the Ito-Girsanov expression, $\sum_i \overline{\Delta}_i$ is unconstrained; in the continuous-time limit, $\sum_i \overline{\Delta}_i \Rightarrow 0$. The conclusion must be that although Ito's lemma is valid in infinite dimensions, its use in finite dimensions creates instabilities in numerical schemes based on the Ito-Girsanov expression, Eq. (5).

The resulting paths (not shown here) using the psHMC method look like a noisy version of the so-called MPP [39]. In particular, for the first 95% of its length, the path can be described as an OU process in the narrow well. In the last 5% of the path, a transition is made into the broad well. Note that this probability advantage increases exponentially as the path length increases.

To explore the instability, it is instructive to use a spectral representation, that is to rewrite the path in terms of a sine transform, namely

$$x_t = x_0 + \frac{t}{T}(x_T - x_0) + \sqrt{\frac{2}{T}} \sum_n \frac{a_n}{\omega_n} \sin(\omega_n t), \tag{10}$$

with $\omega_n = n\,\pi\,/\,T$. In the psHMC method the effective Hamiltonian can be expressed as

$$H_{\text{eff}} = \frac{1}{2}\sum_n a_n^2 + \frac{1}{2\,\epsilon}\int_0^T dt\; G(x_t) + \frac{1}{2}\sum_n b_n^2, \tag{11}$$

with b_n being the momentum conjugate to a_n. Hamilton's equation for the (algorithmic) time evolution is

$$\frac{\partial b_n}{\partial \tau} = -a_n - \frac{1}{2\,\epsilon}\sqrt{\frac{2}{T}}\int_0^T dt\; \frac{\sin(\omega_n t)}{\omega_n}\,\frac{\partial G}{\partial x}. \tag{12}$$

Remember that an underlying condition when using Ito's lemma was the noise history and the positions remain uncorrelated. The consequence of this condition is that the coefficients $\{b_n\}$ are i.i.d., since they are related to the sine transform of the noise. For those frequencies where the second term on the right-hand side of Eq. (12) dominates, the algorithm pushes the path to the minimum of the (effective) energy, which is an unphysical result. To remain in the physical regime, the second term on the right-hand side of Eq. (12) must be small compared to the first. For large frequencies, the second term is indeed small. For intermediate frequencies, if the path length T is not large enough, the second term will dominate. At the lowest frequencies, since $\omega_n = n\,\pi\,/T$, when T is large then the second term dominates in Eq. (12). Although this is not a rigorous proof, it looks as though, for any path length T and nonzero Δt, an instability exists.

At low temperatures, a particle spends exponentially long times in a metastable energy basin before hopping over the confining barrier. It was hoped that one could sample short transition paths, thereby bypassing these long waiting times. Using the Ito-Girsanov expression in such a method evidently fails spectacularly. It is surprising that instability in the numerics comes from the low, rather than high, frequency contributions. Should not the time increment, Δt, play an important role? As Δt shrinks, the multiplicity begins to override the variation in the Ito-Girsanov expression. However, for any nonzero value of Δt, one has thrown away an infinite number of frequencies and a corresponding number of degrees of freedom. The multiplicity that remains does not seem to be sufficient to override the variation. We have failed to design an algorithm on a finite grid that honors the assumption made by using Ito's lemma. And we do not see a way to ameliorate the catastrophe produced when using the Ito-Girsanov expression on a finite-time grid. It remains an open question if it is indeed possible to do so. It may be that we have to turn to other approaches, such as the one by Orland and coworkers [43].

VII. RANDOM WALK METROPOLIS

We now turn to another way of eliminating the effects of the troublesome cross term, given in Eq. (8). By eliminating correlations between the noise and the position, one can ensure that $\sum_i \overline{\Delta}_i \Rightarrow 0$. We can do this by using a simple sampling method, the random walk metropolis (RWM) algorithm, which restricts the region of path space being explored. We use RWM to sample $\overline{\mathbb{P}}_p$, Eq. (5), proceeding as follows: First, create a Brownian path that starts and ends at the origin. A new Brownian bridge is generated and then combined with the current path (with the sum of the squares of the

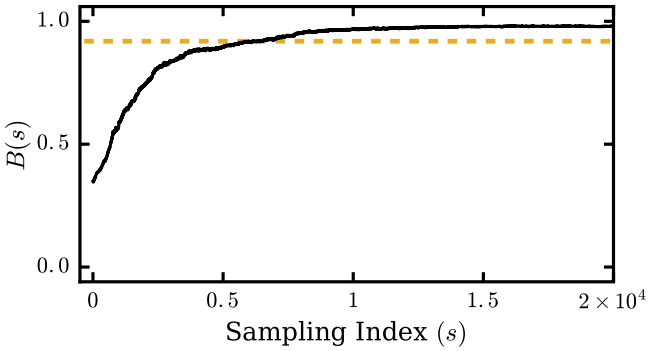

FIG. 4. Results for the calculation using the RWM algorithm starting from a randomly generated Brownian bridge. As a function of iteration number, a plot of the fraction of the path which resides in the broad well (black curve) and the equilibrium value (dotted line).

mixing coefficients being unity). A proposed path is generated from the Brownian bridge by shifting the starting point to be $x_0 = 0.4$ and the ending point to be $x_T = 1.6$. The acceptance or rejection of this new path is based on $\overline{\mathbb{P}}_p$ [Eq. (5)]. This procedure was repeated thousands of times and generated the results displayed in Fig. 4. As shown in this figure, the starting Brownian bridge evolves to a path that is concentrated in the broad well. The fraction of the time that the path spends in the positive half plane begins at a value below 0.40 and settles to a value larger than 0.95. This result differs from the sampling of the Ito-Girsanov expression using the psHMC method, as shown above, because the noise in a Brownian Bridge is not correlated with the path position (by construction). In the absence of correlations, the discrete version of Ito's lemma is obeyed to sufficient accuracy to avoid the instabilities shown in Eq. (12).

VIII. CONCLUSION

In this paper, we examined algorithms designed for sampling pinned diffusion paths using the continuous-time limit of the Onsager-Machlup functional. The OM functional is based on Brownian dynamics and provides a way of understanding the double-ended path-sampling problem [13]. It had been accepted that in the continuous-time limit, the Onsager-Machlup functional could be replaced by the Ito-Girsanov change of measure [Eq. (5)] in computational algorithms as a way of handling the infinities inherent in such a limit. We have shown here that this is inappropriate. First, direct sampling gives unphysical results when using the same values of the algorithmic parameters, which produced sensible results using methods based on finite sums, Eq. (3) or Eq. (7). Second, interpreting the Ito-Girsanov change of measure as a probability distribution favors some paths over others even though paths of the same duration must have the same probability. Numerical algorithms, being finite-dimensional, fail to capture this effect when using the Ito-Girsanov path measure.

It was previously observed that the MPPs for many potentials appeared to be unphysical [39], which should have been taken as an indication that something was amiss. Now we understand why. To derive the Ito-Girsanov expression, Eq. (5) as the continuous-time limit of the OM functional, Eq. (3), one uses Ito's lemma, which assumes that noise and positions are not correlated. In this limit any variation in the measure is overwhelmed by the infinite degrees of freedom inherent in the continuous-time process. However, when determining a MPP, one is asking for the *optimal noise* for a path subject to the boundary conditions. This question and the assumption are in opposition. The MPP is indeed optimal in some sense, but its construction is based on violating the above assumption. We therefore conclude that the MPP is unphysical as it is no longer related to the original SDE where the noise must be spatially and temporally uncorrelated, i.e., unoptimized.

For example, we now see that the results for the Γ-limit for a particle moving in the two-dimensional potential studied by Pinski *et al.* [44] can also be reinterpreted as a consequence of the same phenomena. Namely, the generalization of Eq. (3) to two dimensions (x and y) would have each Cartesian component being separately squared. Thus, the large-deviation [45] paths follow the gradients of the potential. When progressing to the continuous-time limit and using the Ito-Girsanov expression, the (quadratic) structure is lost and one can find maximizers that follow an equipotential line instead [44], where the x component of the force combines with the y component of the displacement (and vice versa). Such maximizers exist only when the noise and the path are correlated, which, as we noted above, is unrelated to the original SDE. Such maximizers are contained in the Ito-Girsanov formula only because one has disregarded the overwhelmingly dominant path multiplicity. When using the Ito-Girsanov expression, Eq. (5), one finds that catastrophic damage can be done to the integrity of the sampling method.

We would like to emphasize that the use of the original OM functional, Eq. (3), is an appropriate method for exploring paths that describe barrier hopping. One can generate physical ensembles of paths using Eq. (3), but these algorithms may be computationally demanding as the full Hessian is required, rather than the Laplacian in the continuous-time case. Such algorithms still need development before they can become useful.

The theory of classical path integrals is very similar to Feynman's approach to quantum mechanics [46]. In calculating quantum path integrals, the classical path is the most probable as it corresponds to the minimum action. The quantum action is a complex number and the phase plays the crucial role. In the vicinity of the classical path the phase is stationary. The contributions to the propagator from paths that are close to the classical path are the same to second order in the path differences. The total contributions to the propagator from paths that are far away from the classical path are small due to cancellations cause by the phase factors. The difference then is that the classical path integrals are not complex, all contributions are real, and the most probable diffusion path is not a physical entity.

The consequences of the ideas presented in this article reach deep into the literature. Here is a partial list, by no means comprehensive, of the works affected by our results: For probing the folding of proteins, several works [1,8–10,47,48] suffered from using the Ito-Girsanov as a path measure in a finite-dimension path space or from placing too much importance on MPPs. The use of the OM functional as the foundation of a thermodynamic action which can be minimized

is noted in many general articles such as McKane's entry [49] in an encyclopedia, reviews by Touchette [32], by Smith [2], and by Qian [4]. As indicated above, the action is derived from noise produced by the thermal bath, which has no knowledge of the system that is under study. The noise, and thus the action, is unphysical for an optimized path. The work of Speck *et al.* [3] uses the optimal trajectory in explaining the role of entropy production. Using the optimal trajectory as a starting point, they found that a "kink" in the action is smeared out by fluctuations. This is consistent with our conclusion, but we go a step further and indicate that the action itself is completely flat when all the effects of fluctuations are included.

To conclude, we reiterate an idea of Still *et al.* [50], who examined the flow of information in a system evolving through a stochastic process. Any information flow is a direct result of the response of the environment to the changes in the system. In ideal Brownian dynamics, the heat bath does not respond to such changes, and thus no information flows. And as we have shown here, the absence of this feedback ensures that noise is never optimized, that the "action" cannot be minimized, and the most probable path is a misnomer as it rarely occurs.

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