

# Enhanced long-term simulation of Hamiltonian systems containing a strong non-convex potential

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## **Abstract**

Many physical systems exhibit rapid motion coupled to a slowly varying motion. Often the rapid motion is associated with a stiff contribution in the potential energy function. In this context, the situation typically considered in the literature is the one with a strictly convex potential. Under some technical assumptions, one can then show that the slow motion is reproduced by a properly constrained system. In this paper we are concerned with a different situation: Often different time-scales can be found because of many local minima and barrier crossing between these minima. We suggest here to replace the detailed motion in the minima and the local barrier crossings by a statistical model which is then coupled to the slow equations of motion over long periods of time. This leads to Langevin type equations of motion subject to an appropriate time transformation.

# 1 Introduction

In this paper we consider Hamiltonian systems containing a strong potential. Such systems arise, for example, in the context of molecular dynamics (MD). To make those systems mathematically tractable, we formally introduce the Hamiltonian

$$H(q, p) = \frac{p^t M^{-1} p}{2} + V(q) + U_\epsilon(q/\epsilon)$$

with  $\epsilon$  a small parameter  $1 \gg \epsilon > 0$  and  $V(q)$  as well as  $U_\epsilon(q)$ ,  $\epsilon \geq 0$ , smooth functions. The corresponding equations of motion are

$$\frac{d}{dt}q = M^{-1}p, \tag{1}$$

$$\frac{d}{dt}p = -\nabla V(q) - \frac{1}{\epsilon}\nabla U_\epsilon(q/\epsilon). \tag{2}$$

and the solutions exhibit rapid motion on time-scales of order  $\epsilon$  due to the force term

$$F_{\text{strong}}(q) = -\frac{1}{\epsilon}\nabla U_\epsilon(q/\epsilon).$$

If the equations of motions are directly discretized by an explicit method such as Verlet [17], then the step-size  $\Delta t$  has to satisfy  $\Delta t \sim \epsilon$  which leads to extremely long simulation times.

In various previous publications [8],[10],[15] it has been assumed that  $U_\epsilon$  is a convex function with the minima condition

$$\nabla U_\epsilon(q/\epsilon) = 0$$

defining a  $m$ -dimensional smooth sub-manifold  $\mathcal{M}$  of the coordinate space  $q \in \mathbb{R}^n$ . Then, under some additional technical assumptions, the dynamics can be reduced to a constrained Hamiltonian systems on the tangent space  $T\mathcal{M}$  of  $\mathcal{M}$  in the limit  $\epsilon \rightarrow 0$  [16], [6], [8]. This eliminates the highly oscillatory components in the solutions and the constrained equations of motion can be discretized by the SHAKE modification [10] of the Verlet scheme using a step-size  $\Delta t \gg \epsilon$ .

In this paper we are concerned with the situation that  $U_\epsilon$  possesses many local minima that are separated by an average barrier height  $E_b$ . In this case

we will again observe rapid motions on a time-scale  $\tau_s \sim \epsilon$  and, on top of this, transitions between nearby local minima over time-scales of length [16]

$$\tau_e \sim \exp\left(\frac{E_b}{k_B T}\right) \tau_s.$$

Here we are interested in the case

$$\delta := \exp\left(\frac{E_b}{k_B T}\right) \gg 1. \quad (3)$$

Thus a diffusion process over length-scales of order  $O(1)$  will require a time-scale of order  $O(\delta)$  which again, simulated as such, would lead to extremely long simulations.

For example, in the context of molecular dynamics [1], bond-stretching and bond-angle bending potentials can be treated as convex potentials of type  $U_\epsilon(q/\epsilon)$  [8], [9]. In contrast to this, the torsion potentials and the Lennard-Jones potentials give raise to non-convex contributions in  $U_\epsilon(q/\epsilon)$ . These contributions can be defined by applying the Gaussian transform of a potential energy function as used in optimization of molecular conformations [18]. Specifically: Let  $f(x)$ ,  $x \in R^n$ , be some function, then its Gaussian transform  $F_\lambda f$  is defined by

$$(F_\lambda f)(x) = \frac{1}{(4\pi)^{n/2} \lambda^n} \int_{R^n} f(y) \exp\left(-\frac{\|y-x\|^2}{4\lambda^2}\right) dy \quad (4)$$

where  $\lambda \geq 1$  is a parameter. Now let  $W(q)$  be some given potential energy function. Then we define the smooth part  $V(q)$  of  $W(q)$  by  $V(q) := (F_\lambda W)(q)$ ,  $\lambda = 1/\epsilon$ , and the non-smooth part by  $U_\epsilon(q/\epsilon) := W(q) - V(q)$ . This splitting is then used in (1)–(2).

In this paper we suggest an enhanced simulation technique based on a statistical model for the motion on time-scales of the local transition time  $\tau_e$ . This corresponds to motions on a length-scale of order  $O(\epsilon)$ . We will show that via such an approach the effective simulation time can be reduced by a factor of  $\delta$  or more. A statistical model for the fast motion seems reasonable whenever one is not interested in the details of the motion on the fast time-scales but, instead, is interested in the qualitative long-term behavior of the system. This leads one to the concept of time-averaging [13], [8]. In Section

7, we discuss this in the context of our simplified equations of motion and show that time-averaging leads to the standard Langevin equations

$$\begin{aligned}\frac{d}{dt}Q &= M^{-1}P, \\ \frac{d}{dt}P &= -\nabla V(Q) - \gamma P + \xi\end{aligned}$$

in the smoothed variable  $(Q(t), P(t))$ .

Based on Liouville's equation [1] and an appropriate initial distribution of states, a different approach to the enhanced simulation of systems like (1)–(2) has been pointed out in [12]. There a nonstationary thermal embedding is used to spatially average over the potential  $U_\epsilon(q/\epsilon)$ .

## 2 A simple statistical model for the fast motion

In this section we investigate the fast motion on length-scales of order  $O(\epsilon)$ . To do so, we consider the canonical coordinate transformation

$$\begin{aligned}Q &= q/\epsilon, \\ P &= \epsilon p\end{aligned}$$

together with the time transformation

$$\tau = t/\epsilon.$$

In the new coordinates  $(Q, P)$  the equations of motion are now

$$\begin{aligned}\frac{d}{d\tau}Q &= M^{-1}P/\epsilon, \\ \frac{d}{d\tau}P/\epsilon &= -\epsilon\nabla V(\epsilon Q) - \nabla U_\epsilon(Q)\end{aligned}$$

and, for small enough  $\epsilon$ , the weak force term

$$F_{\text{weak}}(Q) = \epsilon\nabla V(\epsilon Q)$$

can be dropped from the equations. Finally, we scale the momenta such that  $P/\epsilon \rightarrow P$  and obtain the equations

$$\begin{aligned}\frac{d}{d\tau}Q &= M^{-1}P, \\ \frac{d}{d\tau}P &= -\nabla U_\epsilon(Q).\end{aligned}$$

For notational simplicity, we drop from now on the subscript  $\epsilon$  in  $U_\epsilon(Q)$  and write simply  $U(Q)$ .

Let us assume that this system is locally in thermal equilibrium, i.e., the relative probability  $p_{12}$  of finding the system in the two nearby states  $Q_1$  and  $Q_2$  is equal to the ratio

$$p_{12} = \frac{\exp(-U(Q_1)/(k_B T))}{\exp(-U(Q_2)/(k_B T))}. \quad (5)$$

Furthermore, we assume that the system is ergodic in the sense that trajectories  $(Q(\tau), P(\tau))$  spend the same relative amount  $p_{12}$  of time near the two states  $Q_1$  and  $Q_2$ . This leads us to the following idea: Let  $(\bar{Q}(\bar{\tau}), \bar{P}(\bar{\tau}))$  be a completely random trajectory in phase space  $R^{2n}$ . Then, for this trajectory, the relative probability  $p_{12}$  of visiting the two states  $Q_1$  and  $Q_2$  is equal to one. However, upon performing the differential time transformation

$$d\tau = \exp(-U(Q(\tau)/(k_B T)) d\bar{\tau}$$

along the trajectory  $(\bar{Q}(\bar{\tau}), \bar{P}(\bar{\tau}))$ , the relative probability  $p_{12}$  for the time-transformed trajectory  $(\bar{Q}(\tau), \bar{P}(\tau))$  is now again equivalent to the above expression (5) for the original system. This can be seen from

$$\begin{aligned}\langle f \rangle &= \lim_{T \rightarrow \infty} \frac{\int_0^T f(\bar{Q}(\tau)) d\tau}{\int_0^T d\tau}, \\ &= \lim_{T \rightarrow \infty} \frac{\int_0^T f(\bar{Q}(\bar{\tau})) \exp(-U(\bar{Q}(\bar{\tau})/(k_B T)) d\bar{\tau}}{\int_0^T \exp(-U(\bar{Q}(\bar{\tau})/(k_B T)) d\bar{\tau}}, \\ &= \frac{\int f(Q) \exp(-U(Q)/(k_B T)) dQ}{\int \exp(-U(Q)/(k_B T)) dQ}.\end{aligned}$$

where  $f(Q)$  is an arbitrary observable, for example,  $f(Q) = \delta(|Q - Q_i|)$ ,  $i = 1, 2$ , and  $\delta(x)$  Dirac's delta function.

Thus we are lead to consider the following statistical model for the fast motion on length-scales of order  $O(\epsilon)$ : Define the time-scaling factor

$$\rho(Q) := \exp(-U(Q)/(k_B T))$$

and consider the force-free, time-scaled Langevin equations

$$\rho(Q) \frac{d}{d\tau} Q = M^{-1} P, \quad (6)$$

$$\rho(Q) \frac{d}{d\tau} P = -\gamma P + \xi \quad (7)$$

where  $\gamma > 0$  is a small parameter and  $\xi$  is a Gaussian white noise process with variance [1]

$$\langle \xi(\tau) \xi(\tau + \Delta\tau) \rangle = 2k_B T M \gamma \delta(\Delta\tau).$$

### 3 Coupling to the slow motion

The solutions of (6)–(7) can be transformed back to the original variable  $(q, p)$  and the original time  $t$ . After a few formal manipulations, this yields

$$\begin{aligned} \rho(q/\epsilon) \frac{d}{dt} q &= M^{-1} p, \\ \rho(q/\epsilon) \frac{d}{dt} p &= -\gamma p + \xi. \end{aligned}$$

The weak potential  $V(q)$  is now included into this model through

$$\begin{aligned} \rho(q/\epsilon) \frac{d}{dt} q &= M^{-1} p, \\ \rho(q/\epsilon) \frac{d}{dt} p &= -\nabla V(q) - \gamma p + \xi \end{aligned}$$

where we have again assumed that, over time-scales of order  $O(\tau_\epsilon)$ , the force  $F_{\text{weak}}(q) = -\nabla V(q)$  is practically constant.

Upon introducing the differential time-transformation

$$d\bar{t} := dt / \rho(q/\epsilon), \quad (8)$$

this can be considered as standard Langevin dynamics

$$\frac{d}{dt}q = M^{-1}p, \quad (9)$$

$$\frac{d}{dt}p = -\nabla V(q) - \gamma p + \xi \quad (10)$$

in internal time  $\bar{t}$  together with a time-transformation  $\bar{t} \rightarrow t$  which yields then the averaged dynamics of (1)–(2) up to a linear transformation in time. (This is due to fact that  $\rho(q/\epsilon)$  is uniquely determined only up to a multiplicative factor.) In other words, the slow dynamics feels the local barrier crossing due to the fast motion as a corresponding stretching and shrinking of time.

If the factor  $\delta$  in (3) is uniformly close to one for all local minima of  $U(q/\epsilon)$ , then we have  $\bar{t} \approx t$  and the equations (8)–(10) reduce to standard Langevin dynamics.

## 4 The system in thermal equilibrium

A first simple verification of our approach can be achieved by comparing expectation values in thermal equilibrium for the original system (1)–(2) and our simplified system (8)–(10). Let  $f(q, p)$  be some observable. Then, in thermal equilibrium, the macrocanonical ensemble average is given by

$$\langle f \rangle_{\text{ens}} = \frac{\int f(q, p) \exp(-H(q, p)/(k_B T)) dq dp}{\int \exp(-H(q, p)/(k_B T)) dq dp}.$$

With the decomposition of  $H(q, p)$  into a modified Hamiltonian

$$\tilde{H}(q, p) = \frac{p^t M^{-1} p}{2} + V(q)$$

and  $\rho(q/\epsilon) = \exp(-U(q/\epsilon)/(k_B T))$ , this is equivalent to

$$\langle f \rangle_{\text{ens}} = \frac{\int f(q, p) \rho(q/\epsilon) \exp(-\tilde{H}(q, p)/(k_B T)) dq dp}{\int \rho(q/\epsilon) \exp(-\tilde{H}(q, p)/(k_B T)) dq dp}.$$

Upon assuming ergodicity,  $\langle f \rangle_{\text{ens}}$  is equal to the time average

$$\langle f \rangle_{\text{ens}} = \lim_{T \rightarrow \infty} \frac{\int_0^T f(q(\bar{t}), p(\bar{t})) \rho(q(\bar{t})/\epsilon) d\bar{t}}{\int_0^T \rho(q(\bar{t})/\epsilon) d\bar{t}}$$

along solutions  $(q(\bar{t}), p(\bar{t}))$  of the system (9)–(10) with Hamiltonian  $\tilde{H}(q, p)$ . Now, as done before, we only have to introduce the differential time-transformation

$$dt = \rho(q(\bar{t})/\epsilon)d\bar{t}$$

and the desired result

$$\langle f \rangle_{\text{ens}} = \lim_{T \rightarrow \infty} \frac{\int_0^T f(q(t), p(t)) dt}{\int_0^T dt}$$

follows.

A somewhat similar approach, called umbrella sampling [1], is sometimes taken in the computation of ensemble averages through Monte-Carlo methods. There the potential energy function is modified such that good sampling is achieved and the average is taken over an appropriately modified observable [1].

## 5 Numerical discretization

A simple time-discretization of (8)–(10) is given by the following modified Verlet scheme [1]:

$$q_{n+1} - 2q_n + q_{n-1} = -(\Delta\bar{t})^2(\nabla V(q_n) + \gamma p_n - \xi_n), \quad (11)$$

$$p_n = M \frac{q_{n+1} - q_{n-1}}{2\Delta\bar{t}}, \quad (12)$$

$$t_{n+1} = t_n + \rho(q_n/\epsilon)\Delta\bar{t} \quad (13)$$

and  $q_n$ ,  $n = 0, 1, \dots, N$ , is the approximation to the solution of (1)–(2) with  $q_0 = q(0)$  at  $t = t_n$  up to a linear transformation in time.

This scheme still requires a time-step  $\Delta t \sim \epsilon$  and evaluation of  $\nabla V(q)$  in each time-step to resolve the time-transformation (8) accurately. This frequent evaluation of  $\nabla V(q)$  can be avoided by applying the idea of multiple time-stepping [14]. Let  $L$  be an integer such that  $\Delta T = L\Delta t$  is an appropriate time-step for the slow force  $-\nabla V(q)$ . The multiple time-stepping algorithm consists then of the steps

$$q_{n+1} - 2q_n + q_{n-1} = -(\Delta\bar{t})^2(\gamma p_n - \xi_n),$$

$$p_n = M \frac{q_{n+1} - q_{n-1}}{2\Delta\bar{t}},$$

$$t_{n+1} = t_n + \rho(q_n/\epsilon)\Delta\bar{t}$$



whenever  $n$  is not a multiple of  $L$  and

$$\begin{aligned} q_{n+1} - 2q_n + q_{n-1} &= -(\Delta\bar{t})^2(L\nabla V(q_n) + \gamma p_n - \xi_n), \\ p_n &= M \frac{q_{n+1} - q_{n-1}}{2\Delta\bar{t}}, \\ t_{n+1} &= t_n + \rho(q_n/\epsilon)\Delta\bar{t} \end{aligned}$$

for  $n = iL, i = 0, 1, \dots, N/L$ . Another possibility is to keep  $\nabla V(q_n)$  constant over  $L$  steps in (11)–(13), i.e.,

$$\nabla V(q_n) = \nabla V(q_k)$$

for  $k = iL$  and  $n - k < L$ . However, this leads to a non-reversible discretization. For a more detailed discussion of multiple time-stepping algorithms see [4]).

## 6 An example

Consider the function

$$W(x) = \frac{K}{2}x^2 + \tau \sin(\omega x),$$

$x \in \mathbb{R}$ . Its Gaussian transform (4) is

$$(F_\lambda W)(x) = \frac{K}{2}x^2 + \tau \exp(-\frac{1}{4}\omega^2 \lambda^2) \sin(\omega x).$$

Thus, for  $\omega\lambda \rightarrow \infty$ ,  $(F_\lambda W)(y) = Kx^2/2$ .

Let us now consider the Hamiltonian

$$H(q, p) = p^2/2 + W(q).$$

A splitting into the smooth and non-smooth contribution is simply given by  $V(q) := (F_\lambda W)(q)$  and  $U_\epsilon(q/\epsilon) := W(q) - V(q)$  with  $\epsilon = 1/\omega$  and  $\lambda \geq 1$ . The corresponding equations of motion are now solved using standard Langevin dynamics

$$\begin{aligned} \frac{d}{dt}q &= p, \\ \frac{d}{dt}p &= -\nabla V(q) - \frac{1}{\epsilon}\nabla U_\epsilon(q/\epsilon) - \gamma p + \xi \end{aligned}$$

and compared to the results obtained by using the technique described in this paper. In both cases a heat-bath coupling parameter  $\gamma = 0.5$  was chosen and both systems were started from the initial condition  $(q, p) = (1, 0)$ . Furthermore,  $\lambda = 5$ ,  $\omega = 3.0$ ,  $\tau = 1.0$ ,  $k_B T = 0.5$ , and  $K = 0.2$ . Fig. 1 shows a trajectory  $q(t)$  of the system (1)–(2). A trajectories  $q(t)$  for the splitted potential with  $\alpha = 5.0$  and using the equations (8)–(10) can be found in Fig. 2. The same trajectory as a function of the internal time  $\bar{t}$  is given in Fig. 3. In Fig. 4 the transformed time  $t$  is plotted as a function of the internal time  $\bar{t}$ . Note that, except for local variations, we have  $t \approx \bar{t}$  and that the time-average of  $\rho(q(\bar{t})/\epsilon)$  must be therefore close to one. This will be discussed in more detail in the following section. We also tested a modified scaling function

$$\rho(q/\epsilon) = \exp(-cU_\epsilon(q/\epsilon)/(k_B T))$$

where  $c \geq 1$  is a constant. For  $c > 1$ , this modified  $\rho$  leads to more pronounced localized states near the minima of  $U_\epsilon(q/\epsilon)$ . This can be seen by comparing Fig. 5 ( $c = 5$ ) and Fig. 2 ( $c = 1$ ).

## 7 Averaging in time

Let us assume that the shortest period in the motion of (1)–(2) due to the potential  $V(q)$  is of order  $O(1)$ . In contrast to this, the potential  $U_\epsilon(q/\epsilon)$  contributes high-frequency terms with period of order  $O(\tau_\epsilon)$ ,  $\tau_\epsilon \sim \delta\epsilon$ . In our simplified system (8)–(10) we have replaced the exact fast motion by a statistical model system. However, in many cases one might not even be interested in the statistical behavior on time-scales of order  $O(\tau_\epsilon)$  but only wants to compute the “average” behavior of the system over time-scales of order  $O(1)$ . In this case one can apply the idea of averaging in time [11], [13], [8]. Specifically: To separate the high frequency components from the slowly varying solution components, we introduce the smoothing operator

$$\langle w \rangle_\alpha(t) := \frac{1}{\alpha} \int_{-\infty}^{+\infty} \psi\left(\frac{t-t'}{\alpha}\right) w(t') dt' \quad (14)$$

with  $0 < \alpha \ll 1$  and  $w : R \rightarrow R$ . Here  $\psi : R \rightarrow R$  is an appropriate weight function [8]. One could, for example, chose for  $\psi$  the Meyer scaling

function [3]. Note that, in the frequency domain, the smoothing operator (14) corresponds to a low pass filter with cut-off frequency  $\omega_c = O(1/\alpha)$ .

The idea is now to replace the rapidly varying solutions  $q(t)$  of (1)-(2) by  $\langle q \rangle_\alpha(t)$  with

$$1 \gg \alpha \gg \tau_e$$

and then to seek an approximation to the smooth  $\langle q \rangle_\alpha$  rather than to the rapidly varying  $q(t)$ . We call the functions  $\langle q \rangle_\alpha(t)$ , corresponding to solutions  $q(t)$  of (1)-(2), the *smoothed dynamics* of (1)-(2). In the sequel we will denote  $\langle q \rangle_\alpha(t)$  by  $Q(t)$  and  $\langle p \rangle_\alpha(t)$  by  $P(t)$ .

Since it is not obvious how to obtain the correct averaged equations of motion from the original system (1)-(2), we apply the smoothing operator (14) to the simplified system (8)-(10). By our smoothness assumption on the potential  $V(q)$ , averaging in (9)-(10) is trivial and we obtain

$$\begin{aligned} \frac{d}{dt}Q &= M^{-1}P, \\ \frac{d}{dt}P &= -\nabla V(Q) - \gamma P + \xi \end{aligned}$$

with an appropriately modified  $\gamma$  and corresponding Gaussian white noise process  $\xi$ , i.e.,

$$\langle \xi(\bar{t})\xi(\bar{t} + \Delta\bar{t}) \rangle = 2k_B T M \gamma \delta(\Delta\bar{t}).$$

This leaves us with averaging the differential time-transformation (8), i.e., with

$$dt = \langle \rho(q(\bar{t})/\epsilon) \rangle_\alpha d\bar{t}.$$

Remember (see Fig. 4), in the previous section we had

$$\langle \rho(q(\bar{t})/\epsilon) \rangle_\alpha \approx 1.0.$$

This can be explained as follows: Provided the assumption of local ergodicity holds, the time-average over a time-scale of order  $O(\alpha)$  can be replaced by the spatial average over a length-scale  $l$ ,  $1 \gg l \gg \epsilon$ . This spatial averaging

can be performed by applying the Gaussian transform (4) to  $\rho(q/\epsilon)$  with  $\lambda = 1/l$ . Thus

$$\begin{aligned}\langle \rho(q(\bar{t})/\epsilon) \rangle_\alpha &\approx (F_\lambda \rho)(q) \\ &\approx \exp(-(F_\lambda U)(q)/(k_B T)) \\ &\approx 1\end{aligned}$$

where we have assumed that  $(F_\lambda U)(q) \approx 0$ . This leaves us with the averaged equations of motion

$$\frac{d}{dt}Q = M^{-1}P, \tag{15}$$

$$\frac{d}{dt}P = -\nabla V(Q) - \gamma P + \xi \tag{16}$$

which are just the standard Langevin equations without any time-transformation. The equations (15)-(15) are easy to solve numerically [1] and the computational savings compared to solving (1)-(2) or (8)-(10) are obvious.

## 8 Summary

We have considered Hamiltonian systems containing a strong non-convex potential. This implies motion on different time-scales. If one is only interested in the slow dynamics, one might replace the “exact” fast dynamics by a simplified system. The results of this paper can be considered as a first attempt in this direction. We suggested a very simple model for the fast subsystem based on the assumption that the fast system is in thermal equilibrium. More sophisticated models could be obtained using transition rate theory [5]. Also, the coupling between the fast and slow system could be modeled differently. This will be the subject of further research. Finally, we also considered time-averaging in (8)-(10) and derived the time-averaged equations (15)-(16). Again, these time-averaged equations of motion have to be considered as a crude approximation to the exact  $\langle q \rangle_\alpha(t)$ . The approximation could be improved by replacing the Gauss transform by some more appropriate integral transform [3].

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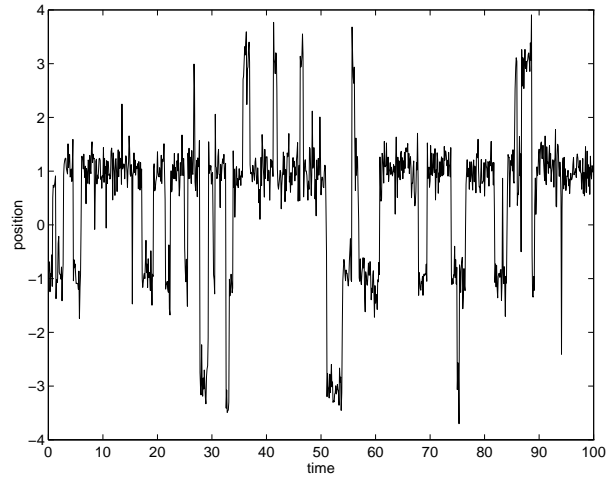


Figure 1: A trajectory  $q(t)$  of the original system.

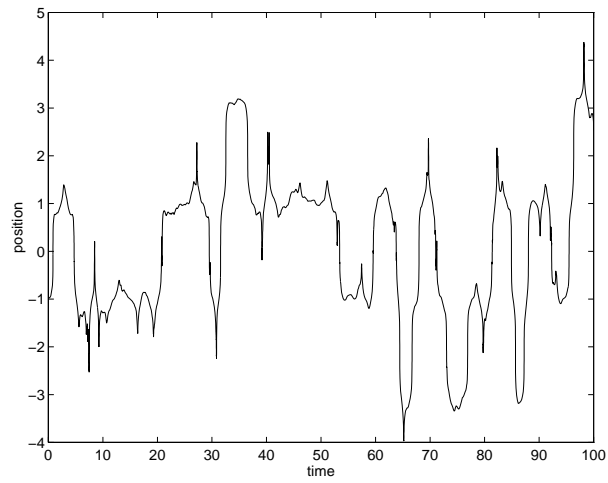


Figure 2: A trajectory  $q(t)$  of the simplified system ( $c = 1$ ).

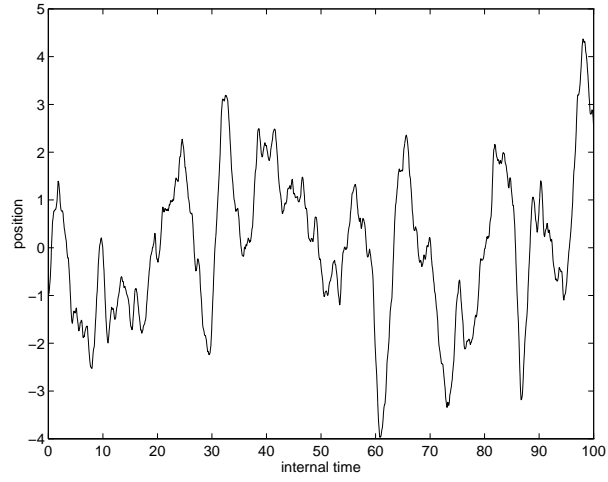


Figure 3: Same trajectory as in Fig. 2 but as a function of the internal time  $\bar{t}$ .

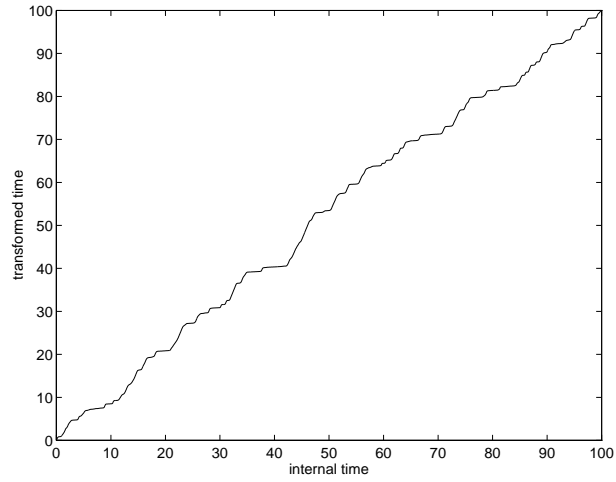


Figure 4: Transformed time  $t$  vs. internal time  $\bar{t}$ .



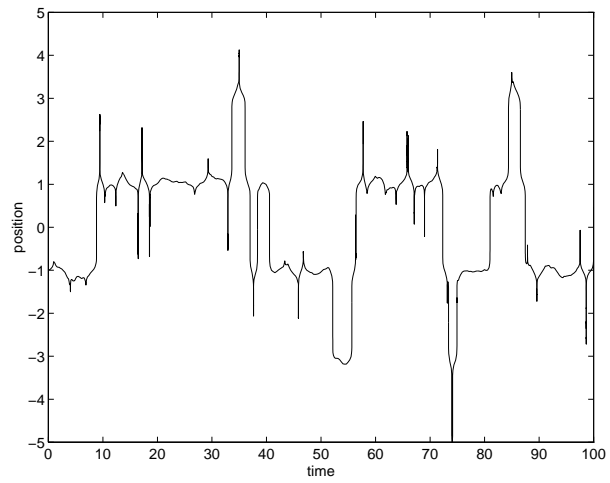


Figure 5: A trajectory  $q(t)$  of the simplified system using the modified time transformation ( $c = 5$ ).