The Construction of Double-Ended Classical Trajectories

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Abstract

In the present paper we describe relaxation methods for constructing double-ended classical trajectories. We illustrate our approach with an application to a model anharmonic system, the Henon-Heiles problem. Trajectories for this model exhibit a number of interesting energy-time relationships that appear to be of general use in characterizing the dynamics.
I. INTRODUCTION

As commonly formulated, problems in classical dynamics are typically “initial value” in character. That is, they involve the determination of the evolution of a set of coordinates and momenta given their values at a specified starting time. Assuming the relevant equations of motion are known, this problem reduces to the numerical task of integrating these equations forward for the required time period. Although not without technical challenge, such initial value problems are well posed and amenable to study with established methods [1].

In certain physical applications, however, “double-ended” formulations of the dynamics prove more natural. These include, for example, the establishment of chemical transition states [2], the search for mechanisms of complex reactions [3], and various semiclassical and quantum formulations of dynamics [4–6]. It is more appropriate in these applications to specify the initial and final positions for the trajectory rather than initial positions and momenta. Since double-ended boundary conditions do not, in general, determine a unique path, there may be zero, one, or many such trajectories for a specified transit time.

Less developed than their initial value counterparts, the most common technique for generating double-ended paths basically amounts to trajectory “shooting.” In this approach the required paths are established by varying initial trajectory momenta in order to find all values that lead to the desired final positions. Viable for relatively simple low-dimensional problems, this procedure is cumbersome for general applications where “aiming” problems become severe.

Relaxation methods for the construction of double-ended trajectories have been discussed by Doll, Beck and Freeman [7]. Related developments have been presented more recently by Gillilan and Wilson [8]. We review and extend our original discussion in Section II below and describe a brief application to model, anharmonic problem, the Henon-Heiles system, in Section III.
II. FORMAL DEVELOPMENTS

We adopt a one-dimensional notation in what follows as a matter of convenience noting that the generalization to many-dimensional applications is straightforward.

We seek the classical path(s) for a one-dimensional conservative system with a known potential energy, $V(x)$, that begin at the point $x$ at time zero and end at the point $x'$ a time $t$ later. To proceed it is convenient to write the paths in terms of a dimensionless time, $u$, that ranges from zero to unity. In terms of this dimensionless time, an arbitrary path of the type we seek can be written as

$$x(u) = x + (x' - x)u + \sum_{k=1}^{\infty} a_k \sin(k\pi u).$$

(1)

The straight line portion of Eq. (1) builds the required boundary conditions into the description while the remaining Fourier sum describes all possible fluctuations about this reference path. Formally an infinite sum, the number of Fourier terms required in Eq. (1) to obtain convergence in practice varies with application and generally increases with the duration of the trajectory.

The desired classical path(s) are obtained by substituting the path ansatz into the functional,

$$S([x(u)]) = t \int_{0}^{1} du \left\{ \frac{m}{2t^2} \left( \frac{dx(u)}{du} \right)^2 - V(x(u)) \right\},$$

(2)

and requiring that the resulting action be stationary with respect to the expansion coefficients,

$$\frac{\partial S}{\partial a_k} = 0.$$  

(3)

This leads to the non-linear equations for the Fourier coefficients,

$$a_k = -\frac{t^2}{m\pi^2 k^2} f_k(a).$$

(4)

Here $m$ is the particle’s mass and $f_k$ is the $k$th Fourier sine component of the force along the path specified by the coefficients $\{a_k\}$.
\[ f_k(a) = 2 \int_0^1 du \sin(k\pi u) \left( -\frac{\partial V(x(u))}{\partial x(u)} \right). \]  

(5)

We can also arrive at Eq. (4) by substituting Eq. (1) directly into Newton’s equations of motion. The action formulation is more useful, however, since it easily generalizes to finite temperature situations where it is convenient to regard the time variable as a complex quantity \[ \text{[6]} \]. Moreover, the time derivative of the action, a quantity that is easily constructed in practice, provides a convenient measure of the path’s energy. Specifically, the energy of a classical path, \( E_{\text{path}} \), can be expressed as \[ \text{[9]} \]

\[ \frac{\partial S}{\partial t} = -E_{\text{path}}, \]  

(6)

which from Eqs. (1) and (2) is easily shown to be

\[ \frac{\partial S}{\partial t} = -(S/t + 2 \int_0^1 V(x(u))du). \]  

(7)

As noted above, we have flexibility with respect to the choice of the functional form used to describe the classical path. Rather than the Fourier ansatz in Eq. (1), for example, we could utilize the positions of the trajectory at intermediate times as the path variables. Gillilan and Wilson’s recent approach \[ \text{[8]} \] to the double-ended trajectory problem is based on such a “Trotter-like” construction. As with analogous path-integral applications \[ \text{[6]} \], the choice of path description is somewhat arbitrary. We note, however, that Eq. (1) has a number of convenient features. Unlike segmented path constructions, for example, the ansatz specified by Eq. (1) is continuous at all levels of truncation. Moreover, Fourier path expansions avoid problems associated with “stiff” degrees of freedom that are produced in Trotter constructions of high order. The present approach also introduces a convenient set of length scales into the problem. In particular, we see from Eq. (4) that the higher order coefficients (large \( k \)) tend toward zero (i.e. become free-particle like) as \( k \) is increased for \( t \) fixed if the Fourier sine component, \( f_k \), is bounded. Conversely, at sufficiently long times the low-order Fourier coefficients tend to lie on the hypersurfaces defined by \( f_k(a) = 0 \). Finally, Eq. (4) makes explicit certain relationships \[ \text{[10]} \] that are somewhat less obvious within.
other formulations. For example, if the potential involved is characterized by a strength parameter, $\epsilon$, and a natural length scale, $\sigma$, then from Eq. (4) we see that the combination $\epsilon t^2/m\sigma^2$ is a similarity parameter for the associated dynamics. That is, systems having a common value of this parameter possess physically similar trajectories.

The equations for the expansion coefficients (Eq. (4)) are self-consistent in that these coefficients both determine and depend on the force along the path. If the potential energy involved is quadratic (or less), then the equations that determine these coefficients are linear and hence have at most a single solution. For more general potentials, however, the equations are nonlinear and multiple paths are possible. The determination of the required double-ended classical paths is thus reduced to solving the set of self-consistent equations denoted by Eq. (4).

It is useful to recast the classical dynamics problem (the solution of Eq. (4)) as an equilibrium minimization problem involving a fictitious “potential” energy in a higher-dimensional space. Specifically, defining the function $\chi(a)$ as

$$\chi(a) = \sum_{k=1}^{\infty} \epsilon_k^2 \left( a_k + \frac{t^2}{m\pi^2 k^2} f_k(a) \right)^2,$$  

where the $\epsilon_k$ variables are arbitrary real constants, we see that the desired dynamical information (the Fourier coefficients that determine the classical path(s)) corresponds to the global minima (zeroes) of this auxiliary “potential” energy. The topology of $\chi(a)$ dictates the nature of the dynamical solution: a single zero implies only one double-ended trajectory exists for the specified conditions whereas multiple zeroes imply that many such trajectories are present. When they exist, we are often interested in devising strategies for moving between regions of $\chi(a)$ that correspond to different paths [4-6,11]. With this in mind, we note that we have control of the height of “barriers” separating such minima since we are at liberty to vary the constants $\{\epsilon_k\}$ appearing in Eq.(8).

We have utilized traditional minimization [12] and annealing methods [13] as well as quantum annealing techniques [14-16] to locate the required minima of Eq. (8). This latter method locates minima of specified functions (in this case $\chi(a)$) using ground state diffusion
Monte Carlo techniques. It is interesting to note that when used in the present context such techniques amount to a ground state quantum-mechanical approach to classical dynamics. Attempting to solve nonlinear equations through minimization procedures of any type is often ill-advised since it is difficult to distinguish local and global minima of the objective function. Here, however, the solution(s) we seek correspond to zeroes of the function in question and are thus easily distinguished from local minima.

III. NUMERICAL APPLICATION AND DISCUSSION

To illustrate the ideas discussed in the previous section, we examine the dynamics of a model, two-dimensional anharmonic system, the Henon-Heiles problem. In this model, a particle of unit mass is assumed to move on the potential energy surface defined by

\[
V(x, y) = \frac{1}{2}x^2 + \frac{1}{2}y^2 + xy^2 - \frac{1}{3}x^3. \tag{9}
\]

The physical potential is characterized by a shallow minimum \((V(0, 0) = 0)\) and three symmetrically located saddle points \((V(1, 0) = V(-1/2, \pm \sqrt{3}/2) = 1/6)\). Small amplitude vibrational frequencies of note are those for motion about the origin (two degenerate frequencies equal to unity) and that for vibrations perpendicular to the dissociation path at the saddle points (equal to \(\sqrt{3}\)).

A convenient device for summarizing the dynamical information is a two-dimensional display of the energies of the various classical paths (c.f. Eqs. (6) and (7)) plotted as a function of the trajectory duration. The topology of the resulting energy-time plot reflects the character of the dynamics and the underlying potential energy surface. Such figures, presented below, were constructed pointwise from roughly 10^5 individual energy-time values, each obtained using the minimization procedures discussed in Section II starting from randomly chosen values for the expansion coefficients. The number of Fourier coefficients used was increased in each case until convergence of the resulting plot was achieved.

Figure (1) is representative energy-time plot for trajectories that begin and end at a common point, taken here to be the origin, \((x = 0, y = 0)\). Such plots change in detail
but not in basic computational complexity as the initial/final trajectory position is varied. Each of the curves in Fig. (1) represents a distinct type of classical trajectory for the model system. For example, the $E = 0$ line in Fig. (1) corresponds to trajectories where the particle remains motionless at the potential minimum. Such trivial solutions ($\{a_k\} = 0$, all $k$) are always possible when the beginning/end point of the path is an extremum of the potential.

We see that the complexity of Fig. (1) increases with time as new solutions appear. Broadly speaking, these new solutions emerge as primary or secondary branches from the $E = 0$ solution, or as features that descend from energies above the classical threshold, $E = 1/6$. This second class of solutions resides principally (but not exclusively) above the dissociation threshold. Figure (1) is a summary of the distinct energies for paths that satisfy the required double-ended boundary conditions at various times. It indicates both the total number of such paths, and the number that fall within a particular energy range. The latter information is central in deciding which paths are relevant to the dynamical process of interest for finite temperature systems.

To understand the general character of the various features, it is useful to note that if the potential were purely harmonic, normal mode vibrations would give rise to a series of vertical lines in Fig. (1) at half-integer multiples of the natural periods for small amplitude motion. Such solutions would have an infinite slope ($dE/dt = \infty$) since the period for harmonic motion is independent of its energy. Recalling that the normal mode frequencies for present system are unity, we identify the features emerging from the zero energy solution at time intervals of $\pi$ as remnants of such small amplitude vibrational motion.

Anharmonic effects modify the small amplitude vibrational features and give rise to the curvature evident in Fig. (1). In particular, the dissociative character of the potential makes possible vibrational motion of arbitrary duration by allowing the system to (essentially) come to rest atop the dissociation barrier. The series of curves asymptotically approaching the dissociation limit, $E = 1/6$, are characteristic of such motion. Distinct differences between the low energy behavior of the features occurring at times equal to odd and even multiples
of \( \pi \) can be understood by recalling the half-period for motion that starts at the potential minimum and is directed at the repulsive (attractive) wall of a typical one-dimensional molecular potential decreases (increases) with increasing energy \([18]\). The two branches of the odd-\( \pi \) features thus reflect an unequal number of inner and outer turning points of the associated anharmonic motion. It is important to note that the low-energy slopes of the vibrational features differ fundamentally from the corresponding harmonic estimates. Finally, from their time spacing and from plots of the associated trajectories, we associate the regular series of features seen emerging from the dissociative branches of the various vibrational solutions in Fig. (1) with trajectories that have oscillations perpendicular to the dissociation channel.

The features that descend from above the dissociation limit \((E = 1/6)\) in Fig. (1) are classical analogs of resonances. If properly oriented, such trajectories can persist for extended periods of time before they find the dissociative portion of the potential energy surface. At certain times (e.g. \(t \approx 15\)), bound motion emerges from this family of solutions. Unlike the previous vibrational features, we see in Fig. (1) that resonance solutions proliferate explosively with increasing time. Similar behavior in more complex systems can also be anticipated in the vicinity of isomerization thresholds.

Figure (2) represents a similar energy-time plot for the Henon-Heiles system, except that unlike Fig. (1) the initial and final positions for the trajectories are distinct. Here the paths begin at the origin, \((x, y) = (0, 0)\), and end at a point beyond the dissociation barrier, \((x', y') = (3/2, 0)\). Since the dissociation is an activated process, there is a minimum energy threshold for such paths and the trivial, zero energy solution is absent. At very short times, motion across the barrier is essentially ballistic and the trajectory energy scales as \(1/t^2\). The left-most branch visible in Fig. (2) corresponds to such a direct dissociative path. The second major branch that descends from \(E = 0.5\) near \(t = 4\) is a similar dissociative path, except that here the particle has suffered a single reflection from the repulsive wall of the potential opposite the dissociation channel. With increasing time, the energies of these and other more involved vibrational trajectories decrease toward a value equal to the
barrier height. Such asymptotic limits thus serve as a measure of the barrier height for dissociation. As in Fig. (1), the series of regularly spaced, near vertical features seen in Fig. (2) are associated with trajectories that undergo oscillatory motion perpendicular to the dissociation coordinate. The “domain” structure seen in the energy-time plots suggests that these and other solutions exhibit a “non-crossing” behavior.

IV. SUMMARY

We have presented methods for the construction of double-ended classical trajectories. Based on Fourier path expansions, the present approach reduces the original dynamical problem to one of finding the minima of a fictitious, high-dimensional classical potential energy. Numerical applications to a model, anharmonic system, the Henon-Heiles potential, reveal a variety of general energy-time relationships for the double-ended trajectories of the system.

For purposes of illustration, the present work has focused on a relatively simple dynamical system. Although the limits of the approach described here are not yet completely established, it is appropriate to note that they extend well beyond the present low-dimensional, model applications. We have found, for example, that using such approaches we can successfully construct various double-ended trajectories for simple atomic clusters of various sizes. These preliminary studies suggest that many of the generic features observed in Figs. (1-2) are present in the dynamics of these more general systems. Details of these cluster applications will be presented elsewhere.

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FIGURE CAPTIONS

1. Figure 1(a) Energy-time plot for the Henon-Heiles system. Paths begin and end at the minimum of the potential and contain up to twelve Fourier coefficients in their description.

2. Figure 1(b) As in Fig. (1a) for longer times to explore the increase in number and complexity of the $E \geq 1/6$ solutions.

3. Figure (2) As in Fig. (1a), except that paths are dissociative in character ($(x, y) = (0, 0), (x', y') = (3/2, 0)$).