

## 1.7 Chaotic Trajectories of Nonlinear Systems

Restricting our study to the curves defined by a system of first integrals and/or the consideration of small oscillations near equilibrium points would greatly limit the range of accessible dynamical phenomena. If we construct a molecular system describing many bodies interacting in nonlinear force laws, there would be no obvious reason to expect that there are many first integrals present to constrain the motion. Indeed, experience indicates that the situation is quite the opposite: typically only the energy and the total momentum of a molecular system are conserved quantities. Thus we are in general left with a complicated dynamical system whose solutions cannot be analytically determined.

*Example 1.8<sup>5</sup> (Planar Lennard-Jones Trimer)* One of the simplest illustrations of the chaotic nature of molecular systems is given by the Lennard-Jones model consisting of just three atoms with motion restricted to the plane. The energy is

$$E = K + U = \frac{\|\dot{\mathbf{q}}_1\|^2}{2} + \frac{\|\dot{\mathbf{q}}_2\|^2}{2} + \frac{\|\dot{\mathbf{q}}_3\|^2}{2} + \hat{\phi}_{\text{LJ}}(\|\mathbf{q}_1 - \mathbf{q}_2\|) + \hat{\phi}_{\text{LJ}}(\|\mathbf{q}_2 - \mathbf{q}_3\|) + \hat{\phi}_{\text{LJ}}(\|\mathbf{q}_1 - \mathbf{q}_3\|),$$

with the interatomic interaction given by  $\hat{\phi}_{\text{LJ}}(r) = 4[r^{-12} - r^{-6}]$ .

The global minimum of this simple system must be radially symmetric. Placing the atoms at the vertices of an equilateral triangle, we have

$$U = 3\hat{\phi}_{\text{LJ}}(r),$$

where  $r$  is the length of a side. This is minimized when  $r = 2^{1/6} \approx 1.1225$ .

In general, when the total potential is a sum of distance potentials

$$U = \frac{1}{2} \sum_{i \neq j} U_{ij},$$

where  $U_{ij}(\mathbf{q}_i, \mathbf{q}_j) = \varphi_{ij}(\|\mathbf{q}_i - \mathbf{q}_j\|)$ , we say that the system has *central forces*. In this case,

$$\frac{\partial}{\partial \mathbf{q}_i} U_{ij}(\mathbf{q}_i, \mathbf{q}_j) = -\frac{\partial}{\partial \mathbf{q}_j} U_{ij}(\mathbf{q}_i, \mathbf{q}_j),$$

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<sup>5</sup>The Lennard-Jones Trimer is included as an example in the **MD.M** package, see <http://MolecularDynamics.info>

and so, for central forces,

$$\sum_{i=1}^N m_i \ddot{\mathbf{q}}_i = \mathbf{0},$$

which expresses the constancy of the momentum. Moreover, viewing the  $\mathbf{q}_i$  as vectors in  $\mathbb{R}^3$  (with 0 as their third component),

$$\mathbf{q}_i \times \frac{\partial}{\partial \mathbf{q}_i} U_{ij}(\mathbf{q}_i, \mathbf{q}_j) = -\mathbf{q}_j \times \frac{\partial}{\partial \mathbf{q}_j} U_{ij}(\mathbf{q}_i, \mathbf{q}_j),$$

which implies

$$\frac{d}{dt} \sum_{i=1}^N \mathbf{q}_i \times (m_i \dot{\mathbf{q}}_i) = \mathbf{0},$$

and tells us that the total *angular momentum* is also conserved. This means that the system will translate and rotate at a constant rate in time.<sup>6</sup> By a judicious choice of initial conditions, the center of mass can be kept at the origin and the net rotation removed. This corresponds to a symmetric configuration which is termed the *isosceles* three body problem (i.e., at all times the atoms are the vertices of an isosceles triangle). The original system had six positional degrees of freedom, but four have now been removed by imposing the momentum constraints. Therefore we would expect a model with just two degrees of freedom. While the conservation of angular and total momentum allow us to remove some of the degrees of freedom of the problem, reducing it to a smaller system, this problem is not integrable.

Let us introduce new coordinates in the Lennard-Jones trimer as illustrated in Fig. 1.21, so that the center of mass is fixed at the origin: that is,

$$\mathbf{q}_1 = \begin{bmatrix} x \\ -y/3 \\ 0 \end{bmatrix}, \quad \mathbf{q}_2 = \begin{bmatrix} -x \\ -y/3 \\ 0 \end{bmatrix}, \quad \mathbf{q}_3 = \begin{bmatrix} 0 \\ 2y/3 \\ 0 \end{bmatrix},$$

reducing the energy to

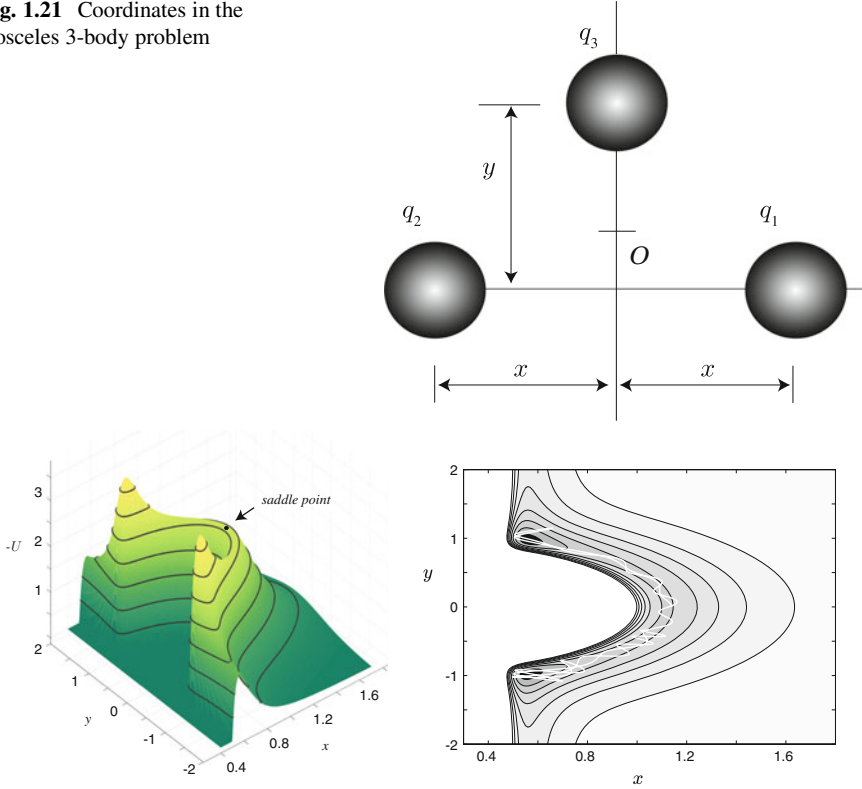
$$E = \dot{x}^2 + \frac{\dot{y}^2}{3} + 2\hat{\varphi}_{\text{LJ}}(\sqrt{x^2 + y^2}) + \hat{\varphi}_{\text{LJ}}(2x),$$

which describes the vibrational motion. Over time the positions will vary within some region in the  $xy$  plane, whose boundary is dependent on the energy  $E$  of the initial condition. What is this boundary? Since the energy is conserved, and the

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<sup>6</sup>Note that in periodic boundary conditions the linear momentum would also be preserved, but the angular momentum is not.

**Fig. 1.21** Coordinates in the isosceles 3-body problem



**Fig. 1.22** *Left*: surface plot of the negative potential energy for the isosceles 3-body problem showing iso-potential curves. *Right*: the level sets of the potential energy function are shown for the isosceles 3-body problem, together with a snapshot of a constant energy trajectory (*light curve*)

kinetic energy is non-negative, we must have

$$2\hat{\phi}_{\text{LJ}}(\sqrt{x^2 + y^2}) + \hat{\phi}_{\text{LJ}}(2x) \leq E.$$

On the left side of Fig. 1.22 are shown the level curves of the potential energy function, with color gradations indicating the energy level between  $-3$  and  $0$ . (When  $E > 0$ , the bodies eventually escape to infinity;  $E < -3$  is not attainable.) Superimposed on the level curves we have shown a short time trajectory (the wiggly white curve).

A surface plot of the **negative of** potential energy is shown on the left in Fig. 1.22. Arranging the three atoms in a collinear configuration ( $y = 0$ ) the potential energy becomes  $\hat{U} = \hat{U}(x) = 2\hat{\phi}_{\text{LJ}}(x) + \hat{\phi}_{\text{LJ}}(2x)$ . Minimizing the potential in the collinear configuration allows us to determine the *saddle point*  $(x_*, 0)$ . Near this point,  $U$  decreases if we move in the  $\pm y$  direction and increases if we move in the  $\pm x$

direction. (For further discussion of the Lennard-Jones few-body problem from a dynamical systems perspective, the reader is referred to [87].)  $\square$

### 1.7.1 Global Solutions

Looking at the trajectories of a molecular dynamics simulation involving even a few atoms (such as the restricted trimer model, above) suggests their erratic, irregular aspect. Individual paths will not be expected to be predictable in any practical sense—every time one atom collides with another it will exchange a small amount of energy and momentum with the other atom, the precise amounts depending in an intricate way on the motions of all the atoms of the system, and the atoms then move on in perturbed directions. In a very short time, the state of the system is well stirred by the molecular interactions. This is one of the elements of the common view of what constitutes a chaotic dynamical system.

In the words of H. Poincaré, writing over a century ago [304],

A very small, unnoticeable cause can determine a visible very large effect; in this case we claim that this effect is the product of random chance. However, even if the natural laws were perfectly known, we would only be able to know the initial conditions with some approximation. If this allows us to know the future with the same approximation that is all we need. We will say that the phenomenon is foreseeable, that it is governed by laws. However this is not always the case, it is possible that a very small initial difference leads to a very large change in the final state. . .

Poincaré's comments probably derived from his understanding of the three-body gravitational problem, but they would apply as well to a typical molecular system.

Typical definitions of a “chaotic dynamical system” [103] require at least the following conditions to be satisfied on the phase space  $\mathcal{D}$ :

- The solutions depend sensitively on the initial data taken from  $\mathcal{D}$ ;
- The flow is topologically transitive in  $\mathcal{D}$ .

Let us address these in turn, without being entirely formal. The sensitive dependence on initial conditions can be taken to mean that if a pair of initial points of phase space is given which are separated by any finite amount, no matter how small, then the gap between these solutions grows rapidly (typically exponentially fast) in time. A problem with this concept is that we often think of molecular systems as having an evolution that is bounded by some sort of domain restriction or a property of the energy function: the exponential growth for a finite perturbation can therefore only be valid until the separation approaches the limits of the accessible region of phase space. In order to be able to make sense of the calculation of an exponential rate in the asymptotic ( $t \rightarrow \infty$ ) sense, we need to consider infinitesimal perturbations of the initial conditions, and this can be made precise by consideration of the Lyapunov characteristic exponents mentioned at the end of this chapter.

The second condition states that given arbitrarily small neighborhoods  $\mathcal{D}_1$  and  $\mathcal{D}_2$  of two different points in  $\mathcal{D}$  then it is possible to find a trajectory that goes