The Action Principle

The form of the Lagrangian is not arbitrary. In fact, it can be derived directly from quantum mechanics using the Feynman path integral formulation (as discussed in statistical mechanics). However, the Lagrangian can be motivated by introducing the so called *action principle*, which states that a particular *functional* of all paths that a particle can take between two points is extremized along the correct classical solution. The classical *action* is defined in terms of the Lagrangian as follows: Consider a system described by generalized coordinates $q \equiv q_1, q_2, ..., q_{3N}$ and velocities $\dot{q} \equiv \dot{q}_1, \dot{q}_2, ..., \dot{q}_{3N}$. Suppose the system moves from point A to point B in time *T*. At *t*=0, the coordinates and velocites have values $\left[q(0), \dot{q}(0)\right]$ and at *T*, $\left[q(T), \dot{q}(T)\right]$. The action is then defined to be

$$S\left[q\right] = \int_0^T L\left(q(t), \dot{q}(t) \right) dt$$

The notation *S*[*q*] indicates that the action is a function of the 3*N* functions $q_1(t), ..., q_{3N}(t)$. That is, *S* depends on all values of these functions between 0 and *T*. Hence, it is called a *functional*. Like an ordinary function, functionals can be differentiated and integrated. However, these operations must be performed with respect to the function(s) the functional depends on, which means the function(s) must be evauated at some particular point when doing the differentiation. Likewise, when integrating a functional, it must be integrated with respect to all values the function can take on in its full range. We shall see, in particular, how the operation of differentiation works in the course of our derivation.

We will now show that, of all possible paths that the system may follow between A and B, the correct path is the one that extremizes the action. In order to show this, let us consider two paths $q(t)$ and $\tilde{q}(t)$ given by

$$\tilde{q}(t) = q(t) + \delta q(t)$$

where $\delta q(t)$ is a small deviation from the path $q(t)$. The path $\tilde{q}(t)$ is required to satisfy the same initial and final conditions of $q(t)$, i.e.

$$\tilde{q}(0) = q(0) \qquad \dot{\tilde{q}}(0) = \dot{q}(0)$$
$$\tilde{q}(T) = q(T) \qquad \dot{\tilde{q}}(T) = \dot{q}(T)$$

This means that the deviation satisfies

$$\delta q(0) = \delta q(T) = 0 \quad \delta \dot{q}(0) = \delta \dot{q}(T) = 0$$

Given these conditions, the problem of extrimizing the action means that we must find where its first derivative is equal to 0. Using a finite difference representation, this means

$$\delta S = S[\tilde{q}] - S[q] = S[q + \delta q] - S[q] = 0$$

Now, since we need to let $\delta q \to 0$, we can expand $S[q + \delta q]$ to first order in δq. Remembering that q and δq are multidimensional, the expansion can be written as

$$\delta S = \int_0^T L\left(q(t), \dot{q}(t) \right) dt + \int_0^T dt \sum_{\alpha=1}^{3N} \left[\frac{\partial L}{\partial q_\alpha(t)} \delta q_\alpha(t) + \frac{\partial L}{\partial \dot{q}_\alpha(t)} \delta \dot{q}_\alpha(t) \right] - \int_0^T L\left(q(t), \dot{q}(t) \right) dt$$

The first and last terms cancel leaving only

$$\delta S = \int_0^T dt \sum_{\alpha=1}^{3N} \left[\frac{\partial L}{\partial q_\alpha(t)} \delta q_\alpha(t) + \frac{\partial L}{\partial \dot{q}_\alpha(t)} \delta \dot{q}_\alpha(t) \right]$$

In order to have an expression that depends only on δq_α, we integrate the second term by parts:

$$\delta S = \sum_{\alpha=1}^{3N} \int_0^T dt \frac{\partial L}{\partial q_\alpha(t)} \delta q_\alpha(t) + \sum_{\alpha=1}^{3N} \frac{\partial L}{\partial \dot{q}_\alpha(t)} \delta q_\alpha(t) \Big|_0^T - \sum_{\alpha=1}^{3N} \int_0^T dt \frac{\partial L}{\partial \dot{q}_\alpha(t)} \delta q_\alpha(t)$$

$$\delta S = \sum_{\alpha=1}^{3N} \int_0^T dt \left[\frac{\partial L}{\partial q_\alpha(t)} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_\alpha(t)} \right) \right] \delta q_\alpha(t)$$

where the boundary term vanishes because $\delta q_\alpha(0) = \delta q_\alpha(T) = 0$. The deviation, $\delta q(t)$ is defined so that it is not exactly 0 for all *t*. Thus, in order that $\delta S = 0$, the term in brackets must vanish. This is the Euler-Lagrange condition:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_\alpha}\right)-\frac{\partial L}{\partial q_\alpha}=0 \qquad \text{(Euler-Lagrange Equation)}$$

Thus, the path that extremizes the action is exactly that which solves the Euler-Lagrange equation, which is the classical path. Thus, the correct solution to the classical equations of motion also extremizes the action.

The action principle is more than just a formal device. It has been used by various groups to study rare events in chemical processes. The articles by R. Elber and coworkers and Passerone and Parrinello show how the action principle can be used in actual computational chemical studies.

Procedure for deriving the state transition equation

The following general procedure can be followed to derive the differential model using Lagrangian mechanics.

1. Determine the degrees of freedom of the system. Establish your generalized coordinated and their derivatives $\left[\left(q_1,\dot{q}_1\right),\ \left(q_2,\dot{q}_2\right),\ \ldots\ \left(q_n,\dot{q}_n\right)\right]$.
2. Express the kinetic energy in terms of your generalized coordinates and their derivatives: KE = $T\left(q_1,\dot{q}_1,q_2,\dot{q}_2,\ldots,q_n,\dot{q}_n\right)$
3. The potential energy is only a function of position, and therefore does not depend on the derivatives of the generalized coordinates: PE = $U\left(q_1,q_2,\ldots,q_n\right)$.
4. Let $L=T-U$ be the Lagrangian function. Write the Euler-Lagrange Equation for *each* of your generalized coordinates and their derivatives:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_1}-\frac{\partial L}{\partial q_1}=0$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_2}-\frac{\partial L}{\partial q_2}=0$$

$$\vdots$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_n}-\frac{\partial L}{\partial q_n}=0$$