so its differential is

$$dF = dU - T\,dS - S\,dT = T\,dS - p\,dV + \sum_j \mu_j\,dN_j - T\,dS - S\,dT$$
$$= -\,p\,dV - S\,dT + \sum_j \mu_j\,dN_j \tag{7.157}$$

which shows that the Helmholtz free energy is a function $F(V, T, \boldsymbol{N})$ of the volume V, the temperature T, and the numbers $\boldsymbol{N}$ of molecules. □

7.13 Principle of Stationary Action in Mechanics

In classical mechanics, the motion of n particles in three dimensions is described by an action density or lagrangian $L(q, \dot{q}, t)$ in which q stands for the $3n$ generalized coordinates $q_1, q_2, \ldots, q_{3n}$ and $\dot{q}$ for their time derivatives. The action of a motion $q(t)$ is the time integral

$$S = \int_{t_1}^{t_2} L(q, \dot{q}, t)\,dt. \tag{7.158}$$

If $q(t)$ changes slightly by $\delta q(t)$, then the first-order change in the action is

$$\delta S = \int_{t_1}^{t_2} \sum_{i=1}^{3n} \left[\frac{\partial L(q, \dot{q}, t)}{\partial q_i}\,\delta q_i(t) + \frac{\partial L(q, \dot{q}, t)}{\partial \dot{q}_i}\,\delta \dot{q}_i(t) \right] dt. \tag{7.159}$$

The change in $\dot{q}_i$ is the time derivative of the change δq_i

$$\delta\,\frac{dq_i}{dt} = \frac{d(q_i + \delta q_i)}{dt} - \frac{dq_i}{dt} = \frac{d\,\delta q_i}{dt}, \tag{7.160}$$

so we have

$$\delta S = \int_{t_1}^{t_2} \sum_i \left[\frac{\partial L(q, \dot{q}, t)}{\partial q_i}\,\delta q_i(t) + \frac{\partial L(q, \dot{q}, t)}{\partial \dot{q}_i}\,\frac{d\,\delta q_i(t)}{dt} \right] dt. \tag{7.161}$$

Integrating by parts, we find

$$\delta S = \int_{t_1}^{t_2} \sum_i \left[\left(\frac{\partial L}{\partial q_i} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} \right) \delta q_i(t) \right] dt + \left[\sum_i \frac{\partial L}{\partial \dot{q}_i} \delta q_i(t) \right]_{t_1}^{t_2}. \tag{7.162}$$

According to the **principle of stationary action**, a classical process is one that makes the action **stationary** to first order in $\delta q(t)$ for changes that vanish at the end points $\delta q(t_1) = 0 = \delta q(t_2)$. Thus a classical process satisfies Lagrange's equations

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0 \quad \text{for} \quad i = 1, \ldots, 3n. \tag{7.163}$$

Moreover, if the lagrangian L does not depend explicitly on the time t, as in **autonomous** systems, then the **hamiltonian** (7.142)

$$H = \sum_i \frac{\partial L}{\partial \dot{q}_i}\, \dot{q}_i \, - \, L \tag{7.164}$$

does not change with time because its total time derivative $\dot{E}$ is the vanishing explicit time dependence of the lagrangian $-\partial L/\partial t = 0$

$$\dot{H} = \sum_i \left(\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i}\right) \dot{q}_i + \frac{\partial L}{\partial \dot{q}_i}\, \ddot{q}_i - \frac{dL}{dt} = \sum_i \frac{\partial L}{\partial q_i}\, \dot{q}_i + \frac{\partial L}{\partial \dot{q}_i}\, \ddot{q}_i - \frac{dL}{dt} = -\frac{\partial L}{\partial t} = 0. \tag{7.165}$$

Equivalently, **the energy** $E = H$ **is conserved**.

The **momentum** p_i **canonically conjugate** to the coordinate q_i is

$$p_i = \frac{\partial L}{\partial \dot{q}_i}. \tag{7.166}$$

If we can write the time derivatives $\dot{q}_i$ of the coordinates in terms of the q_k's and p_k's, that is, $\dot{q}_i = \dot{q}_i(q, p)$, then the **hamiltonian** is a Legendre transform of the lagrangian (example 7.27)

$$H(q, p) = \sum_{i=1}^{3n} p_i\, \dot{q}_i(q, p) - L(q, p). \tag{7.167}$$

This rewriting of the velocities $\dot{q}_i$ in terms of the q's and p's is easy to do when the lagrangian is quadratic in the $\dot{q}_i$'s but not so easy in other cases.

The change (7.162) in the action due to a tiny detour $\delta q(t)$ that differs from zero only at t_2 is proportional to the momenta (7.166)

$$\delta S = \sum_i \frac{\partial L}{\partial \dot{q}_i}\, \delta q_i(t_2) = \sum_i p_i\, \delta q_i(t_2) \tag{7.168}$$

whence

$$\frac{\partial S}{\partial q_i} = p_i. \tag{7.169}$$

We can write the total time derivative of the action S, which by construction

(7.158) is the lagrangian L, in terms of the $3n$ momenta (7.169) as

$$\frac{dS}{dt} = L = \frac{\partial S}{\partial t} + \sum_i \frac{\partial S}{\partial q_i}\,\dot{q}_i = \frac{\partial S}{\partial t} + \sum_i p_i \dot{q}_i. \tag{7.170}$$

Thus apart from a minus sign, the partial time derivative of the action S is the energy function (7.164) or the hamiltonian (7.167)

$$\frac{\partial S}{\partial t} = L - \sum_i p_i \dot{q}_i = -E = -H. \tag{7.171}$$

7.14 Symmetries and Conserved Quantities in Mechanics

A transformation $q_i'(t) = q_i(t) + \delta q_i(t)$ and its time derivative

$$\dot{q}_i'(t) = \frac{dq_i'(t)}{dt} = \frac{dq_i(t)}{dt} + \frac{d\,\delta q_i(t)}{dt} = \dot{q}_i(t) + \delta\dot{q}_i(t) \tag{7.172}$$

is a **symmetry** of a lagrangian L if the resulting change δL vanishes

$$\delta L = \sum_i \frac{\partial L}{\partial q_i(t)}\,\delta q_i(t) + \frac{\partial L}{\partial \dot{q}_i(t)}\,\delta\dot{q}_i(t) = 0. \tag{7.173}$$

This symmetry (7.173) and Lagrange's equations (7.163) imply that the quantity

$$Q = \sum_i \frac{\partial L}{\partial \dot{q}_i}\,\delta q_i \tag{7.174}$$

is **conserved** because its time derivative vanishes

$$\frac{d}{dt}\left(\sum_i \frac{\partial L}{\partial \dot{q}_i}\,\delta q_i\right) = \sum_i \left(\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i}\right)\delta q_i + \frac{\partial L}{\partial \dot{q}_i}\,\frac{d\,\delta q_i}{dt} = \sum_i \frac{\partial L}{\partial q_i}\,\delta q_i + \frac{\partial L}{\partial \dot{q}_i}\,\delta\dot{q}_i = 0. \tag{7.175}$$

Example 7.29 (Noether's theorem for momentum and angular momentum) Suppose the coordinates q_i are the spatial coordinates $\boldsymbol{r}_i = (x_i, y_i, z_i)$ of a system of particles with time derivatives $\boldsymbol{v}_i = (\dot{x}_i, \dot{y}_i, \dot{z}_i)$. If the lagrangian is unchanged $\delta L = 0$ by **spatial displacement** or **spatial translation** by a constant vector $\boldsymbol{d} = (a, b, c)$, that is, by $\delta x_i = a$, $\delta y_i = b$, $\delta z_i = c$, then the momentum in the direction $\boldsymbol{d}$

$$\boldsymbol{P}\cdot\boldsymbol{d} = \sum_i \frac{\partial L}{\partial \boldsymbol{v}_i}\cdot\boldsymbol{d} = \sum_i \boldsymbol{p}_i\cdot\boldsymbol{d} \tag{7.176}$$

is conserved.

If the lagrangian is unchanged $\delta L = 0$ when the system is rotated by an angle $\boldsymbol{\theta}$, that is, if $\delta \boldsymbol{r}_i = \boldsymbol{\theta} \times \boldsymbol{r}_i$ is a symmetry of the lagrangian, then the angular momentum $\boldsymbol{J}$ about the axis $\boldsymbol{\theta}$

$$\sum_i \frac{\partial L}{\partial \boldsymbol{v}_i} \cdot (\boldsymbol{\theta} \times \boldsymbol{r}_i) = \sum_i \boldsymbol{p}_i \cdot (\boldsymbol{\theta} \times \boldsymbol{r}_i) = \left(\sum_i \boldsymbol{r}_i \times \boldsymbol{p}_i \right) \cdot \boldsymbol{\theta} = \boldsymbol{J} \cdot \boldsymbol{\theta} \quad (7.177)$$

is conserved. (Emmy Noether 1882–1935) □

Example 7.30 (Lagrangian's that are functions of the accelerations) If a lagrangian L depends upon the accelerations $\ddot{q}_i$ but not explicitly upon the time, then the equations of motion

$$0 = \frac{\partial L}{\partial q_i} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) + \frac{d^2}{dt^2}\left(\frac{\partial L}{\partial \ddot{q}_i}\right) \quad (7.178)$$

and an analog of the equation (7.165) for $\dot{E}$ imply that the energy

$$E = \sum_i \dot{q}_i \left[\frac{\partial L}{\partial \dot{q}_i} - \frac{d}{dt}\left(\frac{\partial L}{\partial \ddot{q}_i}\right)\right] + \ddot{q}_i \frac{\partial L}{\partial \ddot{q}_i} - L \quad (7.179)$$

is conserved.

□

7.15 Homogeneous First-Order Ordinary Differential Equations

Suppose the functions $P(x, y)$ and $Q(x, y)$ in the first-order ODE

$$P(x, y)\, dx + Q(x, y)\, dy = 0 \quad (7.180)$$

are homogeneous of degree n (Ince, 1956). We change variables from x and y to x and $y(x) = xv(x)$ so that $dy = xdv + vdx$, and

$$P(x, xv)dx + Q(x, xv)(xdv + vdx) = 0. \quad (7.181)$$

The homogeneity of $P(x, y)$ and $Q(x, y)$ imply that

$$x^n P(1, v)dx + x^n Q(1, v)(xdv + vdx) = 0. \quad (7.182)$$

Rearranging this equation, we are able to separate the variables

$$\frac{dx}{x} + \frac{Q(1, v)}{P(1, v) + vQ(1, v)}\, dv = 0. \quad (7.183)$$