
Fundamentals of Classical Mechanics: *From Newton to Hamilton*

1. Newtonian Mechanics

All model solutions of mechanical problems require knowledge of forces, or potentials, and inertias to describe accurately the trajectory of a body from a given initial condition in position and momentum. Newton's elementary formulation is the simplest of several, but only for very simple situations. More complex dynamics can be described more adequately in terms of Lagrangian or *Hamiltonian mechanics*.

In Newton's approach, the motion of a particle of mass (inertia) m along a degree of freedom x , subjected to a potential $V(x)$, is described in terms of an **Equation of Motion** relating the particle's momentum p to the **gradient** of the potential

$$F_x = - \{grad V(x)\}_x = -\partial V / \partial x \quad (1)$$

according to

$$\dot{p}_x = F_x = -\partial V / \partial x \quad (2)$$

Here, $\partial V / \partial x$ denotes the **partial derivative** of V with respect to the variable x , **keeping all its other variables fixed**. The dot over a quantity denotes the derivative with respect to time t , two dots mean the second derivative with respect to time.

In three spatial dimensions, with a position vector $\vec{r} = (x, y, z)$ expressed in terms of Cartesian coordinates x , y , and z , this is generalized to:

$$\vec{F} = -grad V(\vec{r}) = -\vec{\nabla}V(\vec{r}) = -\left\{ \frac{\partial V}{\partial x} \vec{u}_x + \frac{\partial V}{\partial y} \vec{u}_y + \frac{\partial V}{\partial z} \vec{u}_z \right\} \quad (3)$$

where the \vec{u}_i ($i=x,y,z$) are unit vectors in the respective directions. (We write vectors here as "row" vectors, i.e., triplets of numbers in a row, simply because the format fits a written text better. The

notation of column vectors $\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ is completely equivalent, but

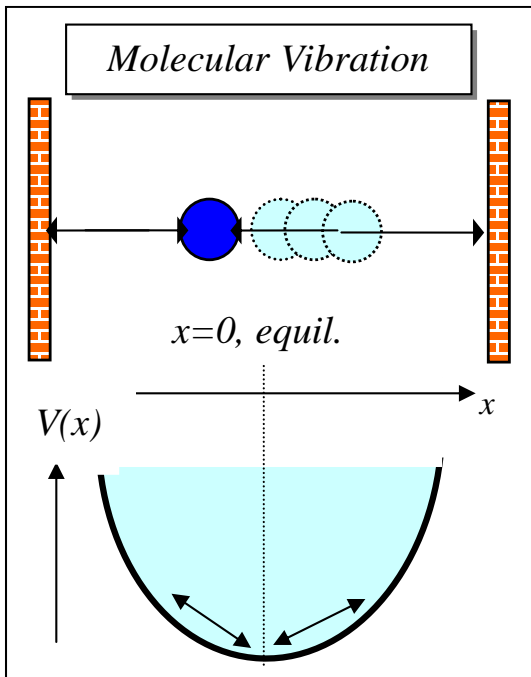
takes more space in print.) The operator $\vec{\nabla}$ is called "del" or "nabla". The equation

$$\dot{\vec{p}} = \vec{F} = -\text{grad}V(\vec{r}) \quad (4)$$

then results as the **fundamental equation (EOM) of Newtonian Mechanics**.

This equation will be illustrated for the simple case of a **Harmonic Oscillator** representing, e.g., a vibrating atom in a linear molecule (bond stretching mode). For simplicity, one replaces the atoms on the left and right by rigid walls, such as shown in the sketch. Furthermore, only small oscillations about the equilibrium position $x = 0$ are to be considered. Then, the restoring force in x -direction is approximately linear and given by

Hooke's Law



$$F = -k \cdot x$$

(5)

Here, $k > 0$ is the restoring-force constant, and the sign of F indicates the direction of its action. The associated potential is given by

$$V(x) = (1/2)kx^2$$

(6)

It is easy to verify that the negative gradient of this potential is indeed equal to Hooke's force.

With the momentum of the vibrating atom given by $p = m\dot{x}$, the

equation of motion reads:

$$dp/dt = F = -kx \quad \text{or} \quad m\ddot{x} = -kx \quad (7)$$

These equations have the oscillatory solutions

$$x(t) = x(t=0)e^{i\omega t} \quad (8)$$

with an **amplitude** $x(t=0)$ and a **phase factor** $e^{i\omega t}$ depending on the **circular frequency**

$$\omega = 2\pi/T = \sqrt{k/m} \quad (9)$$

This frequency is related to the **period** of the oscillatory motion T by $\omega = 2\pi/T$. The larger Hooke's constant and the smaller the mass, the higher is the frequency of vibration of the atom, as expected.

In Equ. (8), the quantity $i = \sqrt{-1} = e^{i\pi/2}$ is the imaginary unit, and $x(t=0)$ denotes the deviation from equilibrium at time $t = 0$. The position of the atom is, of course, a real number and not

complex as suggested by Equ. (8). This equation is, therefore, to be interpreted as a short-hand notation of the real solution. Since the differential equation (7) does not couple (mix) real and imaginary parts of the solution $x(t)$, both the real and imaginary parts, $\mathcal{Re}(x)$ and $\mathcal{Im}(x)$, respectively, are independent solutions of the problem.

For the temporal variation of the momentum, one obtains from differentiation of $x(t)$ in similar short-hand notation

$$\begin{aligned}
 p(t) &= m \dot{x}(t) = -i(m\omega) \exists x(t=0) \mathbf{e}^{-i\omega t} \\
 &= (m\omega) \exists x(t=0) \mathbf{e}^{-i(\omega t + \pi/2)} \\
 (10) \quad & \\
 &= (m\omega) \exists x(t+T/4)
 \end{aligned}$$

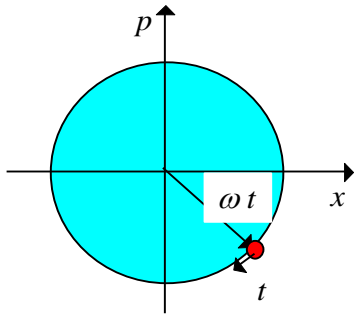
where the '-' sign has been *chosen* to represent a particular physical solution. The last step in (10) comes about since $t + \pi/2\omega = t + T/4$. Together, $x(t)$ and $p(t)$ describe the harmonic oscillation of the vibrating atom. More accurately, both sets

$$[\mathcal{Re}\{x(t)\}, \mathcal{Re}\{p(t)\}] \text{ and } [\mathcal{Im}\{x(t)\}, \mathcal{Im}\{p(t)\}]$$

describe the vibration, each represents a different valid solution. The quantities $x(t=0)$ and $p(t=0)$ are the initial conditions prevailing at $t = 0$. They determine the still open parameters $x(0)$ and $p(0)$. The **boundary conditions** at $t = 0$ may be chosen such that $x(t)$ has a maximum, x_{max} , with $p(t=0) = 0$. But it could be any other possible initial condition.

On the other hand, the momentum $p(t)$ has its maximum *magnitude* (absolute value $p = |\vec{p}|$), p_{max} , at $t=T/4$, where x is zero. Position and momentum of the atom are hence seen to oscillate with the same frequency ω between their maximum positive and negative values, but with a **phase difference** of $\phi = \pi/2 = 90^\circ$. That is, if $x(t)$ is a *sin*-function, then $p(t)$ is a *cos*-function, and vice versa.

*Motion of Harmonic Oscillator
in the Phase Plane*



Hence, the “normalized” system trajectory $\{x(t)/x_{max}, p(t)/p_{max}\}$ prescribes a **unit circle in phase space $\{x, p\}$** . If the oscillation were damped, the trajectory would be a spiral ending in the origin $\{x = 0, p = 0\}$.

The equations of motion for the above dynamical systems are examples of analytically solvable problems. Unfortunately, most dynamical problems of practical interest are not solvable analytically. Then, numerical methods of solution have to be employed. As a simple example, consider the motion of ***N identical particles*** of mass m in our regular 3-dimensional space. The positions of these particles are given by the position vectors $\vec{r}_i = \{x_i, y_i, z_i\}$, their velocity (vectors) by

$$\vec{v}_i = \dot{\vec{r}}_i = \frac{d\vec{r}_i}{dt} = \{\dot{x}_i, \dot{y}_i, \dot{z}_i\} \quad (11)$$

and their acceleration (vectors) by

$$\vec{a}_i = \ddot{\vec{r}}_i = \frac{d\vec{v}_i}{dt} = \{\ddot{x}_i, \ddot{y}_i, \ddot{z}_i\} \quad (12)$$

Using Newton’s equation (3) with the forces $\vec{F}_i(\vec{r}_i)$ acting on the particles, one obtains

$$\frac{d\vec{p}_i}{dt} = m \frac{d\vec{v}_i}{dt} = \vec{F}_i(\vec{r}_i) \quad (13)$$

These are **second-order differential equations** for the coordinates $\vec{r}_i = \{x_i, y_i, z_i\}$ but first order in the velocities. In actual numerical calculations, **sets of two first-order differential equations** (11) and (12) are solved by **linearization** or some other simple approximation. The total considered time interval is divided into finite steps of width Δt , chosen small enough to warrant a **first-order Taylor expansion of the velocities**, such that trajectories are constructed by iteration. For the **x-coordinates** and **x-components of the velocities** of one particular particle, the actually used equations of motion can be written as

$$\begin{aligned}x_{n+1} &= x_n + v_n \Delta t + \frac{1}{2} a_n (\Delta t)^2 \\v_{n+1} &= v_n + \frac{1}{2} (a_{n+1} + a_n) \Delta t\end{aligned}\tag{14}$$

Here, the x-components of the accelerations are defined by the corresponding components of the force acting on the particle at its position at the n th step of the iteration, \vec{r}_n ,

$$a_n = \frac{F_x(\vec{r}_n)}{m}\tag{15}$$

Similar equations can be set up for the other coordinates, y_n and z_n , of the particle considered. All equations have to be integrated simultaneously, step by step, to yield the particle's trajectory. The other particles have to be treated in a similar manner.

2. Lagrangian Approach

In the **Lagrangian Approach**, one derives the equation of motion from the Lagrangian

$$\mathbf{L} = \mathbf{T} - \mathbf{V}$$

(16)

where \mathbf{T} is the kinetic energy and \mathbf{V} the potential energy of the mechanical system. In the following, only an illustration of the equivalence of the Lagrangian and Newtonian methods will be given for the simple case of a point-like particle, since the general derivation of the *Lagrangian* equations of motion is somewhat lengthy. It can be found in texts on classical mechanics, for example in *F. Scheck*.

For this illustration, one starts with the Newton equation (cf. Equ.(2))

$$\dot{p} = F = -\partial V / \partial x \quad (17)$$

in one degree of freedom, x . This equation, a ***mixed second-order differential equation*** is somewhat asymmetric. The left-hand side is proportional to the ***second derivative*** of one function (x with respect to the time t), while the right-hand side is the negative ***first derivative*** of another function (V with respect to x). One can, however, simplify and symmetrize the equation somewhat by realizing that p can be written as a derivative of the kinetic energy $T = p^2 / 2m = (m/2)\dot{x}^2$,

$$p = \frac{\partial T}{\partial \dot{x}} \quad \text{and} \quad \dot{p} = \frac{d}{dt} \frac{\partial T}{\partial \dot{x}} \quad (18)$$

If the potential V is only dependent on the position x and not dependent on the velocity, as is true for many conservative systems, then $\partial V / \partial \dot{x} = 0$. In this case, one can replace the kinetic energy \mathbf{T} in Eq.II.11 by the Lagrangian $\mathbf{L} = \mathbf{T} - \mathbf{V}$, i.e.,

$$p = \frac{\partial T}{\partial \dot{x}} = \frac{\partial L}{\partial \dot{x}} \quad (19)$$

The variable $p = \partial L / \partial \dot{x}$ is called a **generalized** or **canonical momentum**. In many cases, e.g., for conservative systems of rigid bodies, the generalized momentum is equal to the momentum as it is usually defined. Such canonical variables are used in the Hamilton formulation discussed further below.

In addition, usually the kinetic energy T does not **explicitly** depend on the position x , but only on p (or \dot{x}). It only depends **implicitly** on x , i.e., it changes with x only because the momentum p may depend on x through the x -dependence of the potential. Then,

$$\frac{\partial V}{\partial x} = - \frac{\partial L}{\partial x} \quad (20)$$

and, from Newton's equation,

$$\dot{p} = \frac{d}{dt} \frac{\partial L}{\partial \dot{x}} = \frac{\partial L}{\partial x} = F \quad (21)$$

Equ. (21) is equivalent to the **Lagrange Equation**

$$\left\{ \frac{d}{dt} \frac{\partial}{\partial \dot{x}} - \frac{\partial}{\partial x} \right\} L = 0 \quad (22)$$

which is completely equivalent to the Newton equation (7). The Lagrange equation is a **second-order differential equation** for one function (L). For a system with n degrees of freedom, there are n differential equations of the form of Equ. (22), one for each degree of freedom.

Both Newton and Lagrangian equations show some symmetries of the problem in equally simple fashion. For example, if L and, hence, V do not depend on a particular variable x , it follows that

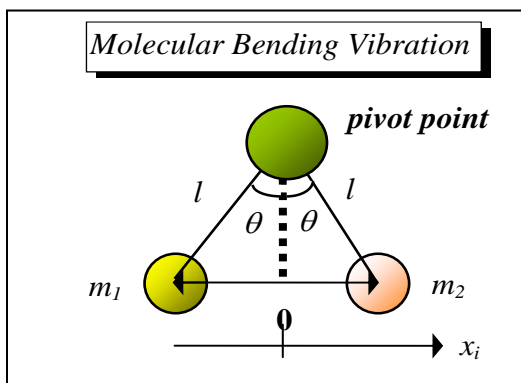
$$\frac{d}{dt} \frac{\partial}{\partial \dot{x}} L = 0 \quad \text{and} \quad p_x = \frac{\partial}{\partial \dot{x}} L = \text{constant} \quad (23)$$

Then, for such a **cyclic variable** x , the associated (generalized) momentum is conserved, i.e., is a **constant of motion**. A trivial example is represented by the one-dimensional oscillator treated earlier. Its equations of motion contain only x and variables associated with x . Therefore, the other spatial coordinates y and z are cyclic, and the momenta in those directions are constants (always $\equiv 0$).

- *The Lagrange equations have one very important advantage over the Newton equations: The former are invariant under coordinate transformation $x \rightarrow \xi$, i.e., they look similar when expressed in either variable x or ξ . For example, this allows one to write down the Lagrange equations for a complex molecule in terms of the so-called normal modes of the molecule, rather than in the separate coordinates of the constituent atoms.*

$$\left\{ \frac{d}{dt} \frac{\partial}{\partial \dot{\xi}} - \frac{\partial}{\partial \xi} \right\} L = 0 \quad (24)$$

How to actually use the Lagrange equations to derive the time-dependence of the position and momentum variables of a system will be illustrated in a simple example of molecular bending-mode vibrations.



Consider the di-atomic molecule (perhaps a sub-cluster of a larger molecule) pictured in the sketch. The atoms of masses m_1 and m_2 , ($= m_1 = m$, for simplicity), are placed in the t -dependent geometry of an equilateral triangle of fixed side length l , where they can pivot about the point at the top of that triangle, changing the distance x between the two atoms. If the

atom-atom interaction is of a van der Waals (Lenard-Jones) type, then there is an equilibrium distance $x = x_0$ between the two atoms, i.e., there is attraction for larger and repulsion for smaller distances.

Assume for simplicity then an **approximate linear** force law,

$$F = -k(x - x_0) \quad (25)$$

with a restoring-force constant $k > 0$. This problem is really one of rotational motion of the atoms at a fixed radius $r = l$ about the pivot point, with the only degree of freedom being the bond angle 2θ . Then, the problem is solved easiest when expressed in that coordinate. First, the force is written in terms of θ and for small deviations about the equilibrium:

$$F = -k l^2 (\theta - \theta_0) \quad (26)$$

with an equilibrium bond angle of $2\theta = 2\theta_0$. This force corresponds to the potential

$$V(\theta) = V(\theta_0) + k l^2 (\theta - \theta_0)^2 \quad (27)$$

without loss of generality, one can set $V(\theta_0) = 0$ in the following calculation.

The kinetic energy of rotation is calculated from the relative velocity $v_\theta = l \dot{\theta}$ of the atoms and their reduced mass

$$\mu = m_1 m_2 / (m_1 + m_2) = m/2 \quad (28)$$

$$T = \frac{\mu}{2} \dot{v}_\theta^2 = \frac{\mu}{2} l^2 \dot{\theta}^2 \quad (29)$$

such that the Lagrangian can be written as

$$L = T - V = 2 \mu l^2 \dot{\theta}^2 - k l (\theta - \theta_0)^2 \quad (30)$$

From direct differentiation of this Lagrangian, the canonical momentum and its time derivative are obtained as

$$\frac{\partial L}{\partial \dot{\theta}} = 4 \mu l^2 \dot{\theta} \quad \text{and} \quad \frac{d}{dt} \frac{\partial L}{\partial \dot{\theta}} = 4 \mu l^2 \ddot{\theta} \quad (31)$$

while the generalized force is calculated as

$$\frac{\partial L}{\partial \theta} = -\frac{\partial V}{\partial \theta} = -2kl \cdot (\theta - \theta_0) \quad (32)$$

Equating the above last two formulas, one obtains finally the equation of motion for the (half) bond angle:

$$\ddot{\theta} = -\frac{k}{2\mu \cdot l} \cdot (\theta - \theta_0) \quad (33)$$

since θ_0 is a constant, and one can subtract $\ddot{\theta}_0$ on the left-hand side and obtains a differential equation for the variable $\ddot{\theta} = \ddot{\theta} - \ddot{\theta}_0$. It has, obviously, oscillatory solutions of the form

$$[\theta(t) - \theta_0] = [\theta(0) - \theta_0] \cdot e^{\pm i \varpi t} \quad (34)$$

with the circular frequency of $\varpi = \sqrt{k/(2\mu l)}$.

3. Hamiltonian Formulation of Mechanics

The Lagrange equation is a *2nd* order differential equation, which is sometimes difficult to solve. However, it can be transformed into a **set of two 1st-order differential equations**, the **Hamilton equations**, which are much easier to integrate. The Hamilton formalism starts from the Hamiltonian

$$H = T + V = 2T - L \quad (35)$$

which gives the **functional dependence** of the total energy on all coordinates $\{q_i\}$ and momenta $\{p_i\}$, where i runs over all degrees of freedom, $\{q_i = x, y, z\}$ and $\{p_i = p_x, p_y, p_z\}$. Here, the generalized coordinates and momenta $p_i = \partial L / \partial \dot{q}_i$ are used, as defined above. $L = T - V$ is the Lagrangian. Since the product of momentum and velocity equals twice the kinetic energy, one can express the Hamiltonian in these terms:

$$H = \sum_i p_i \cdot \dot{q}_i - L \quad (36)$$

The equations of motion are derived from a comparison of all differentials of $H(\{q_i\}, \{p_i\}, t)$ with those of the Lagrangian. The total differential of $L(\{q_i\}, \{\dot{q}_i\}, t)$ is, by definition, written as

$$\begin{aligned} dL &= \frac{\partial L}{\partial t} \cdot dt + \sum_i \left(\frac{\partial L}{\partial q_i} \cdot dq_i + \frac{\partial L}{\partial \dot{q}_i} \cdot d\dot{q}_i \right) = \\ &= \frac{\partial L}{\partial t} \cdot dt + \sum_i (\dot{p}_i \cdot dq_i + p_i \cdot d\dot{q}_i) \end{aligned} \quad (37)$$

The second term in the bracket on the second line can be written as

$$p_i \cdot d\dot{q}_i = d(p_i \dot{q}_i) - \dot{q}_i dp_i \quad (38)$$

and one can reorder terms in Equ. (38) to obtain

$$d\left(\sum_i p_i \cdot \dot{q}_i - L\right) = -\frac{\partial L}{\partial t} \cdot dt - \sum_i (\dot{p}_i \cdot dq_i - \dot{q}_i \cdot dp_i) \quad (39)$$

According to Equ. (36), the left-hand side of this equation represents the **total differential of H**. On the other hand, this differential is, by definition, given by

$$dH = \frac{\partial H}{\partial t} \cdot dt + \sum_i \left(\frac{\partial H}{\partial q_i} \cdot dq_i + \frac{\partial H}{\partial p_i} \cdot dp_i \right) \quad (40)$$

Since all **variables are independent** of each other, one can compare the partial differentials in Eqs. (39) and (40), term by term, i.e., set the corresponding terms equal. One then obtains

Hamilton's Canonical Equations

$$\frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t} \quad \dot{q}_i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (41)$$

These equations are rather symmetric in the variables q_i and p_i , except for the minus sign in the third equation. This sign is due to the fact that the force is given by the *negative* gradient of the potential V .

One simple consequence of Hamilton's equations can be drawn almost right away already from Equ.(40): If **H** does not depend **explicitly** on time, i.e., if the partial t -derivative is zero ($\partial H/\partial t = 0$), then the **total energy is conserved** ($dH/dt = 0$). The total energy is a constant of motion. This is the case, for example, when a system moves under the influence of static (interaction) potentials. The condition is not fulfilled in cases, where the interaction energy is t -dependent, for example, if a molecule is irradiated with a laser (t -dependent electromagnetic radiation).

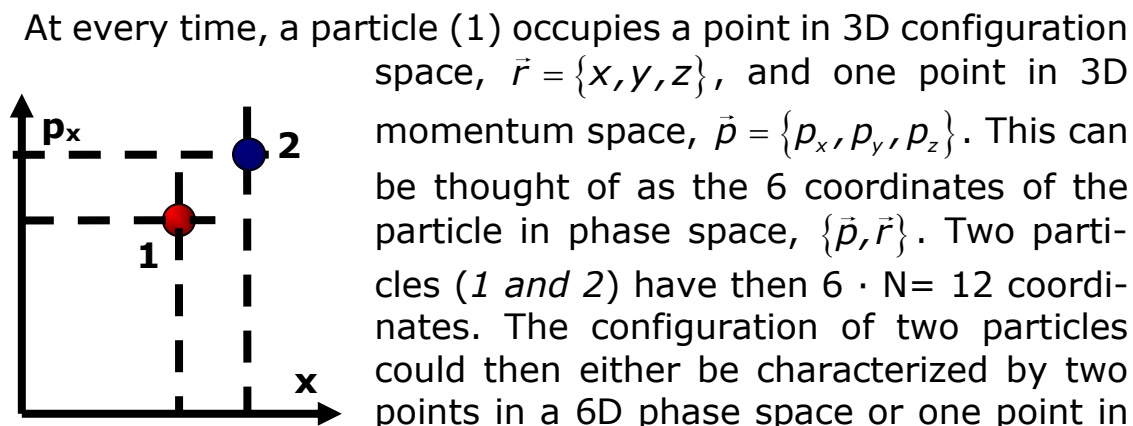
In order to solve a mechanical problem using the Hamilton formalism, one goes through the following procedure:

First one has to construct the functions for the kinetic and the potential energy, using the normal coordinates and momenta.

From these functions, one builds the Lagrangian $L = T - V$ and the Hamiltonian $H = T + V$ and calculates the canonical momenta. This latter step is only then necessary when coordinates and/or momenta appear mixed in kinetic and/or potential terms. Otherwise, normal and canonical momenta are identical.

- *Then, one calculates the Hamiltonian partial derivatives in Equ. (41). These then will provide the equations of motion, as given by Equ.(41).*

The Hamiltonian, more specifically, its dependence on all coordinates and momenta, contains the complete information on a classical system. This pertains in particular to all observables A that describe a classical system, e.g., a system of N particles.



The latter choice turns out to be more convenient, even though it is difficult to represent graphically. Conventionally, one

numbers the spatial and momentum coordinates of all particles in a sequential fashion such that $\{p_i(t), q_i(t); i=1, \dots, 3N\}$ describes the configuration of the N-particle system at time t . This set of time-dependent $6N$ -tuples of coordinates is called the system's phase space trajectory.

For such a system of N particles, there are a number of observables \mathbf{A} of interest, e.g., the total energy E , the position of its center of gravity, $\{X, Y, Z\}$, the total momentum, the summed average values, as well as the spread, etc. As the system evolves in time, so do the values of the observables $A = A(t)$. The observable can have an **explicit time dependence**. Then,

$$\frac{\partial A}{\partial t} \neq 0 \quad (42)$$

But even if there is no explicit t -dependence of \mathbf{A} , its value may change, simply because the system coordinates change. Then, \mathbf{A} has an **implicit t -dependence**. The total temporal rate of change of \mathbf{A} has therefore the following representation:

$$\begin{aligned} \frac{dA}{dt} &= \frac{\partial A}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial A}{\partial q_i} \frac{\partial q_i}{\partial t} + \frac{\partial A}{\partial p_i} \frac{\partial p_i}{\partial t} \right\} = \\ &= \frac{\partial A}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i \right\} \end{aligned} \quad (43)$$

Inserting Hamilton's equations for the time derivatives of coordinates p_i and q_i , one obtains the following expression for the time rate of change of observable \mathbf{A} :

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} \right\} \quad (44)$$

This expression is written usually in short-hand notation, using the Poisson brackets $[\mathbf{A}, \mathbf{H}]$

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + [A, H] \quad (45)$$

which are defined by the two Eqs. (44) and (45).

This rather compact formulation of the time dependence of an observable A demonstrates that in fact the complete information of a classical system of N particles is contained in the system Hamilton function, which in turn defines the t -dependent phase space trajectories.

An important application of the above formalism concerns the time dependence of the phase space density ρ . This is the number of states dN accessible to the system per phase space volume

$$d\Omega = d\Omega_p \cdot d\Omega_q \quad (46)$$

i.e.,

$$\rho = \frac{dN}{d\Omega} \quad (47)$$

In time, all states evolve, for example diverge or converge in phase space, and generally define a new occupied phase space element $d\Omega'$. Each point within the new element $d\Omega'$ is connected to the old element $d\Omega$ by its own trajectory. Hence, the old element is mapped onto the new element by the corresponding system trajectories. This means that

$$\rho(t) = \rho(H\{p_i(t), q_i(t)\}) \quad (48)$$

is a function of the coordinates and momenta, via the Hamilton function H . Therefore, the phase space density ρ is an example of a function A . Therefore, application of formula (45) yields

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] \quad (49)$$

For a conservative system, there is no explicit time dependence of ρ , since there are no phase points created or lost, $\partial\rho/\partial t=0$. Furthermore, one can easily show (homework) that the Poisson brackets for a function of the type of Equ. (48) vanishes also such that one has the famous **Liouville Equation**

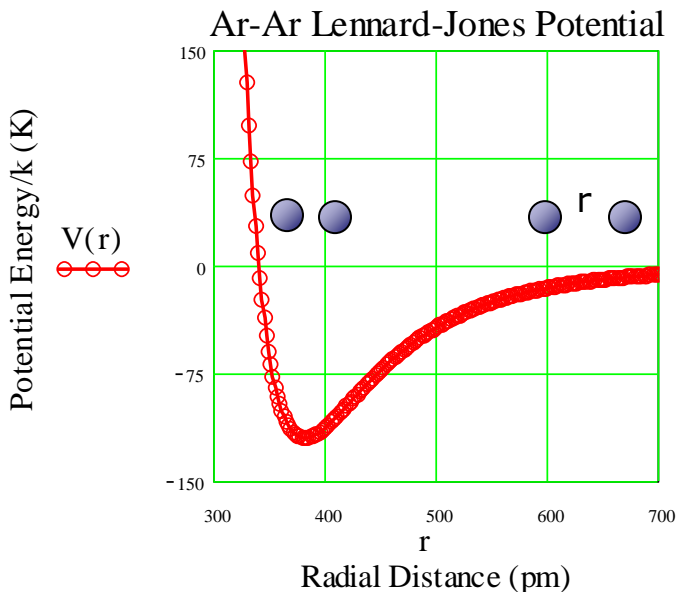
$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + [\rho, H] = 0 \quad (50)$$

implying that the phase space density is constant for a conservative system. Such a statement could not be made for a dissipative system, where frictional forces would lead to a shrinking of the phase space volume occupied by a system.

4. Is Classical Mechanics Deterministic ?

Together with initial conditions, the equations of motion discussed above evolve the system according to a well defined method. However, this does not necessarily imply that the system trajectories are completely predictable. As seen in the first section, chaotic motion can result under various, not always obvious conditions.

Often, such modes are artificially suppressed in theoretical treatments using simplified models.

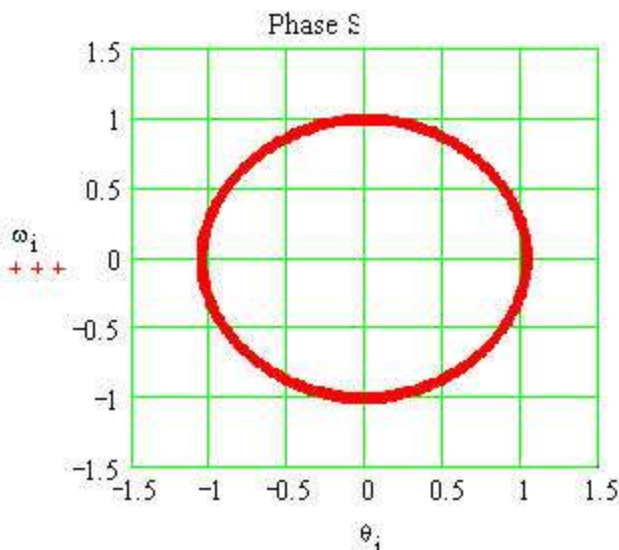


For example, often the interaction potential between two atoms or molecules is approximated as that of a harmonic oscillator. The corresponding force is then replaced by an approximate force that is

linear in the displacement (Hooke's Law (5)). The resulting vibration would then be a perfectly periodic oscillation. [bendingvibes](#)
The phase diagram $\{\dot{r}/\dot{r}_{max}, r/r_{max}\}$ of the vibration would then be a perfect circle. However, the potential is not harmonic. The plot shows a typical form of the interaction potential given by the Lennard-Jones shape for a system of two interacting Ar atoms,

$$V(r) = 4\varepsilon \cdot \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (51)$$

with a strength parameter, given relative to the Boltzmann constant as $\varepsilon/k_B = 120 \text{ K}$, and a range parameter of $\sigma = 341 \text{ pm}$ [$1 \text{ pm} = 1 \times 10^{-12} \text{ m}$]. Since the potential is not strictly quadratic, symmetric about the equilibrium point, the restoring force is not exactly linear in the displacement of the oscillator from its equilibrium position, except for very small displacements and energies close to the ground state of the diatomic Ar-Ar system. For small amplitudes, one obtains circular phase space orbits from direct integra-

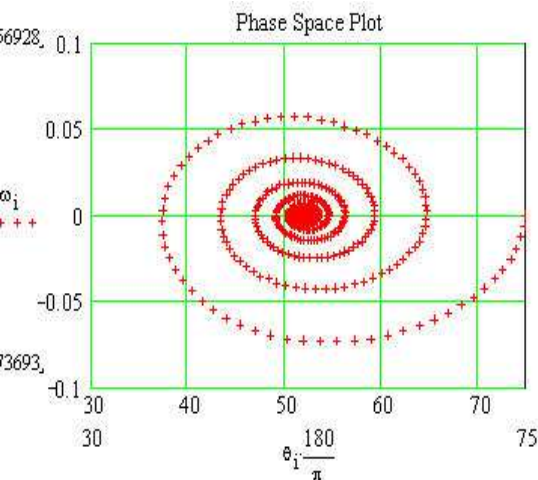


tion of the EOM of the bending mode.

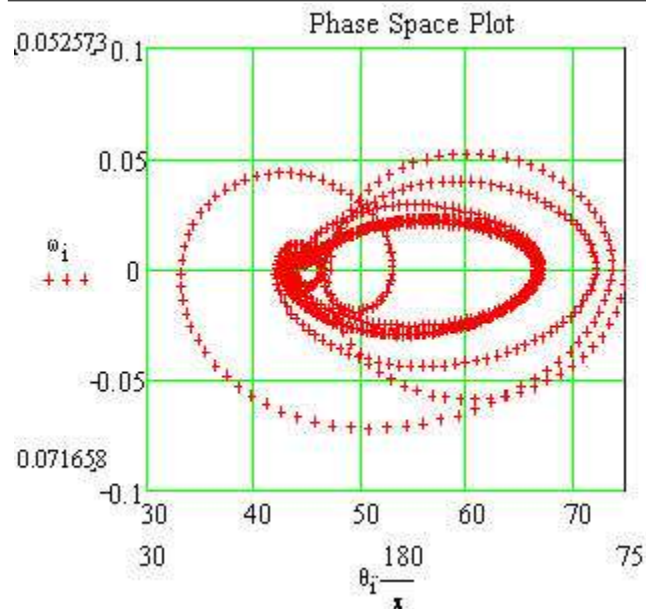
[BendingVibes](#)

In addition, the EOM of the Ar-Ar system could be more complex than the proportionality between conservative force and acceleration implied by Hooke's Law. There could be other influences working on the system due to the environment, for example friction at the neighboring molecules or external electromagnetic fields. Friction leads to a spiraling phase space orbit such as shown in the figure.

Of interest is the response of a realistic damped vibrator to external excitations, such as exerted by weak or strong electromag-

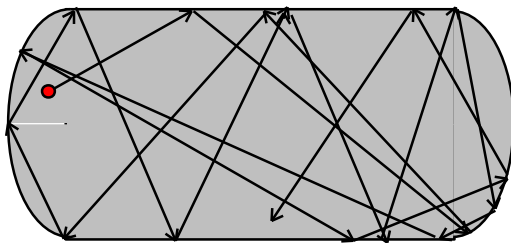
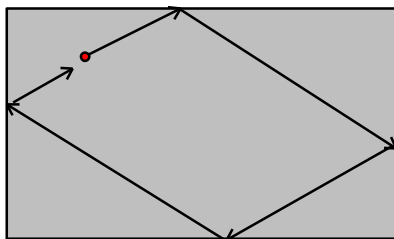


netic fields (optical excitations by laser). Here, one obtains a variety of responses, depending on the relations between conservative, dissipative, and external driving forces. One observes domains with completely orderly motion and others where the bending vibrations show an unexpected, chaotic nature ([BendingVibes-Chaotic](#)). This latter type shows a motion with one or two attractors in phase space.



Random, **chaotic motion** in an ensemble of many particles can

*Periodic and Chaotic Motion
Induced by Scattering*



be induced by different effects. If, a particle is enclosed within a container with irregularly shaped walls, elastic scattering of the particle off the container walls can in effect also induce random motion. This randomness is to be understood in the sense that the particle trajectory will, in time visit every position in the available space (**ergodic behavior**). Such irregularities of the walls are in practice always present. In fact, orderly motion, such as represented by periodic closed orbits have to be considered an exception to the rule. Such orbits only develop for containers with partic-

ular symmetries. The sketch shows the orderly, periodic motion that can result for a particle enclosed in a rectangular vessel with

perfect walls. If the geometry of the vessel is changed into that of a *stadium*, the orbits are no longer periodic and become chaotic, even for perfect container walls. Calculating the density of trajectories over a certain area (or volume) element, one finds a **constant coverage**, given an infinitely long time.