

## 1.2: Phase space

### Hamiltonian Equations of Motion

The Newtonian equations of motion are very convenient for atomistic molecular dynamics (MD) computations. Statistical analysis of trajectories encountered during such MD simulations can be analyzed in terms of thermodynamic quantities, such as free energy. However, for analyzing evolution of the system in terms of spectroscopic properties, the Newtonian description is very inconvenient. Since spectroscopic measurements can provide the most stringent tests of theory, we shall use the Hamiltonian formulation of mechanics in the following. This formulation is particularly convenient for molecules that also have rotational degrees of freedom. For that, we replace the velocity coordinates by momentum coordinates  $p_j = m_j \dot{q}_j$ , where index  $j$  runs over all atoms and for each atom over the three Cartesian coordinates. Furthermore, we assume  $M$  identical molecules, with each of them having  $f$  degrees of freedom, so that the total number of degrees of freedom is  $F = fM$ . Such a system can be described by  $2F$  differential equations

#### Concept 1.2.1: Hamiltonian Equations of Motion

With the single-molecule Hamiltonian  $\mathcal{H}(\mathbf{p}_i, \mathbf{q}_i)$  the equations of motion for  $M$  non-interacting identical molecules with  $f$  degrees of freedom for each molecule read

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial \mathcal{H}(\mathbf{p}_i, \mathbf{q}_i)}{\partial \mathbf{p}_i} \quad (1.2.1)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial \mathcal{H}(\mathbf{p}_i, \mathbf{q}_i)}{\partial \mathbf{q}_i}, \quad (1.2.2)$$

where  $i = 1 \dots M$ . Each of the dynamical variables  $\mathbf{q}_i$  and  $\mathbf{p}_i$  is a vector of length  $f$ . The  $2fM$  dynamical variables span the *phase space*.

#### Definition: Phase Space

*Phase space* is the space where microstates of a system reside. Sometimes the term is used only for problems that can be described in spatial and momentum coordinates, sometimes for all problems where some type of a Hamiltonian equation of motion applies. Sometimes the term *state space* is used for the space of microstates in problems that cannot be described by (only) spatial and momentum coordinates.

If the molecule is just a single atom, we have only  $f = 3$  translational degrees of freedom and the Hamiltonian is given by

$$\mathcal{H}(\mathbf{p}_i, \mathbf{q}_i) = \frac{1}{2m} (p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2), \quad (1.2.3)$$

describing translation. For molecules with  $n$  atoms, three of the  $f = 3n$  degrees of freedom are translational, two or three are rotational for linear and non-linear molecules, respectively, and the remaining  $3n - 5$  or  $3n - 6$  degrees of freedom are vibrational.

### The Liouville Equation

Our observations do not allow us to specify phase space trajectories, i.e. the trajectory of microstates for a single system. Instead, we consider an ensemble of identical systems that all represent the same (observational) macrostate  $\mathcal{O}$  but may be in different microstates. At a given time we can characterize such an ensemble by a probability density  $\rho(\mathbf{p}, \mathbf{q}, t)$  in phase space, where  $\mathbf{p}$  and  $\mathbf{q}$  are the vectors of *all* momentum and spatial coordinates in the system, respectively. We are interested in an equation of motion for this probability density  $\rho$ , which corresponds to the full knowledge that we have on the system. This equation can be derived from an integral representation of  $\rho$  and the Hamiltonian equations of motion.

#### Theorem 1.2.1: Liouville Equation

The probability density  $\rho(\mathbf{p}, \mathbf{q}, t)$  in phase space evolves in time according to

$$\frac{\partial \rho}{\partial t} = \sum_i \left( \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} \right) . \quad (1.2.4)$$

With the [Poisson brackets](#)

$$\{u, v\} = \sum_i \left[ \frac{\partial u}{\partial p_i} \frac{\partial v}{\partial q_i} - \frac{\partial u}{\partial q_i} \frac{\partial v}{\partial p_i} \right] . \quad (1.2.5)$$

this *Liouville equation* can be expressed as

$$\frac{\partial \rho}{\partial t} = - \{ \mathcal{H}, \rho \} . \quad (1.2.6)$$

For the probability density along a phase space trajectory, i.e., along a trajectory that is taken by microstates, we find

$$\frac{d}{dt} \rho(q(t), p(t), t) = 0 . \quad (1.2.7)$$

If we consider a uniformly distributed number  $dN$  of ensemble members in a volume element  $d\Gamma_0$  in phase space at time  $t = 0$  and ask about the volume element  $d\Gamma$  in which these ensemble members are distributed at a later time, we find

$$d\Gamma = d\Gamma_0 . \quad (1.2.8)$$

This is the *Liouville theorem* of mechanics.

## Quantum Systems

Hamiltonian mechanics can be applied to quantum systems, with the Hamiltonian equations of motion being replaced by the time-dependent Schrödinger equation. The probability density in phase space is replaced by the density operator  $\hat{\rho}$  and the Liouville equation by the [Liouville-von-Neumann equation](#)

$$\frac{\partial \hat{\rho}}{\partial t} = - \frac{i}{\hbar} \left[ \widehat{\mathcal{H}}, \hat{\rho} \right] . \quad (1.2.9)$$

In quantum mechanics, observables are represented by operators  $\hat{A}$ . The expectation value of an observable can be computed from the density operator that represents the distribution of the ensemble in phase space,

$$\langle \hat{A} \rangle = \text{Trace} \left( \hat{\rho} \hat{A} \right) . \quad (1.2.10)$$

We note that the Heisenberg uncertainty relation does not introduce an additional complication in statistical mechanics. Determinism had been lost before and the statistical character of the measurement on an individual system is unproblematic, as we seek only statistical predictions for a large ensemble. In the limit of an infinite ensemble,  $N \rightarrow \infty$ , there is no uncertainty and the expectation values of incompatible observables are well defined and can be measured simultaneously. Such an infinitely large system is not perturbed by the act of observing it. The only difference between the description of classical and quantum systems arises from their statistical behavior on permutation of the coordinates of two particles, see Section [\[section:quantum\\_statistics\]](#).

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