

## CLASSICAL SYSTEMS

### TRAJECTORY OF A SYSTEM

time series:

$$q_i(t), p_i(t) \quad i = 1, 3N$$

where the conjugate momenta  $p_i = m_i \dot{q}_i$  and the  $q_i$  are the coordinates for the system.

### PHASE SPACE

6N-dimensional hyperspace

variables:  $3N q_i, 3N p_i$

phase space POINT = STATE of system  
phase space PATH = TRAJECTORY

## PROBABILITY DENSITY FUNCTION

$$\rho = f(\Gamma)$$

where  $\Gamma$  denotes the phase space or a set of phase space variables  $(p, q)$ .

$$\rho(\Gamma)d\Gamma$$

is the number of state points in a small region  $d\Gamma$  about the state point  $\Gamma$

The density function is normalized

$$\int_{\Gamma} d\Gamma \rho(\Gamma) = 1$$

**For the constraints (N, V, T), i.e., for the canonical ensemble, omitting factors  $h^{3N}$ ,**

$$\rho(\Gamma) = \frac{e^{-H(\Gamma)/kT}}{Q}$$

$$Q = \int_{\Gamma} d\Gamma e^{-H(\Gamma)/kT}$$

$$\begin{aligned} H(\Gamma) &= \text{total energy at phase point} \\ &= V_p + T_k \end{aligned}$$

**The normalizing factor  $Q$  is the partition function.**

## PROPERTIES OF A SYSTEM: AVERAGING

The density function  $\rho$  tells us all we can know about a system.

The properties of a system are obtained by averaging, e.g., the thermodynamic variable  $E$ , the energy of a system, is the expectation value

$$E = \langle E \rangle = \int_{\Gamma} d\Gamma \rho(\Gamma) E(\Gamma)$$

For the free energy and entropy of a system,

$$F = -kT \log Q$$

$$S = -k \langle \log \rho \rangle$$

## **ERGODIC HYPOTHESIS**

**The density function  $\rho$  can be obtained by constructing very many copies of a system, each evolving independently and having different starting phase.  $\rho$  is obtained by tallying for this ENSEMBLE of systems, at some instant, the number of systems (states) within  $d\Gamma$  of a phase point  $\Gamma$ .**

**The density function  $\rho$  also can be obtained by following the trajectory of one system for a VERY long time (although no phase point can be revisited, a region of phase space can be revisited).  $\rho$  is obtained by tallying the number of "snapshots" (trajectory points) within  $d\Gamma$  of a phase point  $\Gamma$ .**

**The ERGODIC HYPOTHESIS asserts that the same density function  $\rho$  is found from both the above methods. Thus the trajectory TIME average = the ENSEMBLE average for any variable.**

## **GENERALIZED VARIABLES**

**The Cartesian coordinates and their conjugate momenta are just one set of allowed variables.**

**If appropriate rules are followed, other sets can be constructed.**

**For example, the set of normal coordinates, each of which is independent of the others, and each is a function of one or more of the Cartesian coordinates.**

## **SIMPLIFICATION**

**It is conceptually and mathematically difficult to handle  $3N$  degrees of freedom ( $6N$ -dimensional phase space).**

**The description can be reduced to one of fewer variables by PROJECTION.**

**E.g., to describe the system with a single coordinate, such as a REACTION COORDINATE,  $x$ ,**

$$\rho(x) = \int_{\Gamma} d\Gamma \rho(\Gamma) \delta(x(\Gamma) - x)$$

$\rho(x)dx$  = **probability system near point  $x$**

$$\int_x dx \rho(x) = 1$$

**Information about the system has been lost. How do we account for it? In the ENTROPY, and through use of the FREE ENERGY for description of the reduced-dimensional system.**

## **TIME DEPENDENCE OF THE PROBABILITY DENSITY**

**For an equilibrium system,  $\rho$  is constant and  $d\rho/dt = 0$ . For a non-equilibrium system,  $\rho$  evolves in time, as it must after an external force is applied to a system or after a perturbation is removed from a system. For a classical system,**

$$\frac{d\rho(p, q, t)}{dt} = iL\rho(p, q, t)$$

**where  $iL$  is a differential operator.**