## CLASSICAL SYSTEMS

## TRAJECTORY OF A SYSTEM

**time series:**

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

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

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

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

$H(\Gamma)$ **= total energy at phase point**

**=** $V_p + T_k$

**The normailizing 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**

$$E = < E > = \int_{\Gamma} d\Gamma \, \rho(\Gamma) E(\Gamma)$$

**For the free energy and entropy of a system,**

$$F = -kT \log Q$$

$$S = -k < \log \rho >$$

## 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 of which 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 an operator.**