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 Γ 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 Γ

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

The density function ρ 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). ρ is obtained by tallying the number of "snapshots" (trajectory points) within $d\Gamma$ of a phase point Γ.

The ERGODIC HYPOTHESIS asserts that the same density function ρ 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, ρ is constant and $d\rho/dt = 0$. For a non-equilibrium system, ρ 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.