

**Lecture #30: Modeling intrinsically Stochastic processes. Multiscale Modeling.**

$$I = \frac{\int \int \dots \int f(\underline{q}) w(\underline{q}) d^N q}{\int \int \dots \int w(\underline{q}) d^N q} \quad p(\underline{q}) = \frac{w(\underline{q})}{\int \int \dots \int w(\underline{q}) d^N q}$$

$$I = \int \int \dots \int f(\underline{q}) p(\underline{q}) d^N q$$

$\lim_{N \rightarrow \infty} \frac{\sum_{i=1}^N f(q_i)}{N} = I$  where N is the number of sample points and  $q_i$  is drawn from the partition function  $p(\underline{q})$ .

Will have statistical sampling error  $\delta I_{MC} \approx \sqrt{\frac{\langle f^2 \rangle - \langle f \rangle^2}{N}}$  where  $\langle f^2 \rangle = \frac{\sum_{i=1}^N f^2(q_i)}{N}$

$$dI \approx \frac{1}{\sqrt{N}} \quad \leftarrow \text{does not converge very rapidly}$$

$$\tilde{f} = f - \langle f \rangle_{\text{small}}$$

$$I = \int \int \dots \int \left( \frac{f}{p} \right) p d^N q \quad \rightarrow \text{best weight } p \sim |f|$$

Suppose one samples  $10^6$  points. To obtain an additional significant figure requires  $10^8$  points, so it is difficult to acquire another significant figure. Often, only  $w(\underline{q})$  is known, not  $p(\underline{q})$

**Metropolis Method**

$\{\underline{q}, \dots, \underline{q}_N\}$

randomly choose  $\underline{d}\underline{q}$

if  $w(\underline{q}_N + \delta \underline{q}) \geq w(\underline{q}_N)$

or if  $\text{rand} < \frac{w(\underline{q}_N + \delta \underline{q})}{w(\underline{q}_N)} = \frac{p(\underline{q}_N + \delta \underline{q})}{p(\underline{q}_N)}$

$$\left. \begin{array}{l} \text{if } w(\underline{q}_N + \delta \underline{q}) \geq w(\underline{q}_N) \\ \text{or if } \text{rand} < \frac{w(\underline{q}_N + \delta \underline{q})}{w(\underline{q}_N)} = \frac{p(\underline{q}_N + \delta \underline{q})}{p(\underline{q}_N)} \end{array} \right\} \begin{array}{l} \underline{q}_{N+1} = \underline{q}_N + \delta \underline{q} \\ \text{else} \\ \downarrow \\ \underline{q}_{N+1} = \underline{q}_N \end{array}$$

## System in Thermal Equilibrium

$$p = \frac{e^{-E(q)/k_B T}}{Q(T)} \quad w = e^{-E(q)/k_B T}$$

$$U = \langle E \rangle$$

Ch. 10 of Tester and Modell 1

$$\langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 \frac{d\langle E \rangle}{dT} = k_B T^2 C_V$$

Real systems have fluctuations.

$$\langle N^2 \rangle - \langle N \rangle^2 = k_B T \langle N \rangle^2 K_T / V \quad K_T \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

If the number of particles N is small, the above difference is noticeable.

$$N \pm \sqrt{N} \text{ i.e. } 10^6 \pm 10^3$$

The reason fluctuations do not have to be considered in many systems is  $N = 10^{20}$  or greater. Thus,  $10^{20} \pm 10^{10}$  shows the fluctuations do not affect greatly the significant figures. In nanoscale systems, biological systems, and ignition events, the volumes are small so then fluctuations are noticeable.

## Bayesian Experiments vs. Models

Markov Chain Monte Carlo

$$I = \int \int \dots \int f(Y_{\text{model}}(\underline{\theta})) p(\underline{\theta}) d^N \underline{\theta}$$

## Molecular Dynamics (MD)

Time-Dependent Case, Not at Equilibrium, and Probability Density. Although the equations below are used, they are not correct, because atoms do not move according to Newtonian Mechanics.

Assume in Thermal Equilibrium

$$\frac{dq}{dt} = \frac{-1}{m} \frac{\partial E(q)}{\partial q} + F_{\text{thermal}}(\text{rand})$$

The second term on the right hand side represents a 'kick' to the system.

$$\frac{dq}{dt} = P./m \text{ MatLab Notation}$$

IR "Spectroscopy"

$$100 \text{ cm}^{-1} \rightarrow 3000 \text{ cm}^{-1}$$

$$x - \underline{H}$$

$$\tau_{\text{effect}} \sim 10^0 \text{ s}$$

$$\tau_{\text{fast}} \sim 10^{-14} \text{ s} \text{ "we have a stiffness problem"}$$

Double precision explicit solver  $\rightarrow$  Verlet algorithm

$$(10^{-14})(10^6) \sim 10^{-8} \text{ s} = 10 \text{ nanoseconds}$$

Stiff solvers (need Jacobian), number of variables less than  $10^4$ . Cannot solve biological problems.

Many problems use combined atoms (no hydrogens), remove bond stretches, keep bond torsions and bends.

Be careful of error bars when using these methods.

## **Multiscale modeling**

Unsolved Problem.