University of Washington
Department of Chemistry
Chemistry 553
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Lecture 8: Introduction to Conditional Probabilities
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A. Markov Processes and Conditional Probabilities

- For a completely random process, the condition of a system at a time t is independent of its history so
  $$W_n\left(x_n,t_n;x_{n-1},t_{n-1};\ldots x_0,t_0\right)=W_1\left(x_0,t_0\right)W_1\left(x_1,t_1\right)\cdots W_1\left(x_n,t_n\right) \quad (8.1)$$
- The next level of complexity is called a Markov Process. To define such a process we first define a conditional probability $P_n\left(x_n,t_n\middle|x_{n-1},t_{n-1};\cdots x_1,t_1;x_0,t_0\right)$ *where* $t_0<t_1<\cdots t_n$ which is the probability that a system is at x_n at t_n granted that it was at x_0 at t_0, x_1 at t_1, etc. Some useful properties of joint and conditional probabilities follow…
  - $$W_n\left(x_n,t_n;x_{n-1},t_{n-1};\ldots x_1,t_1;x_0,t_0\right)=P_n\left(x_n,t_n\middle|x_{n-1},t_{n-1};\ldots x_1,t_1;x_0,t_0\right)\times W_{n-1}\left(x_{n-1},t_{n-1};\ldots x_1,t_1;x_0,t_0\right) \quad (8.2)$$
  - Examples
  $$W_2\left(x_1,t_1;x_0,t_0\right)=W_1\left(x_0,t_0\right)P_2\left(x_1,t_1\middle|x_0,t_0\right)$$
  $$W_3\left(x_2,t_2;x_1,t_1;x_0,t_0\right)=W_2\left(x_1,t_1;x_0,t_0\right)P_3\left(x_2,t_2\middle|x_1,t_1;x_0,t_0\right)$$
  (8.3)
- For a Markov process the probability that a system is at x_n at time t_n is only dependent upon its immediate and most recent history.
  $$P_n\left(x_n,t_n\middle|x_{n-1},t_{n-1};\cdots x_1,t_1;x_0,t_0\right)=P_2\left(x_n,t_n\middle|x_{n-1},t_{n-1}\right). \quad (8.4)$$

- For a Markov Process
  $$W_n\left(x_n,t_n;x_{n-1},t_{n-1};\ldots x_1,t_1;x_0,t_0\right)=P_2\left(x_n,t_n\middle|x_{n-1},t_{n-1}\right)\times W_{n-1}\left(x_{n-1},t_{n-1};\ldots x_1,t_1;x_0,t_0\right)$$
  $$\therefore W_2\left(x_1,t_1;x_0,t_0\right)=P_2\left(x_1,t_1\middle|x_0,t_0\right)\times W_1\left(x_0,t_0\right)$$
  (8.5)
- For stationary Markov Processes
  $$P_2\left(x_n,t_n\middle|x_{n-1},t_{n-1}\right)=P_2\left(x_n\middle|x_{n-1},t_n-t_{n-1}\right)=P_2\left(x_n\middle|x_{n-1},\tau\right)$$
  $$\therefore W_2\left(x_1,t_1;x_0,t_0\right)=W_2\left(x_1;x_0,\tau\right)=W_1\left(x_0\right)P_2\left(x_1\middle|x_0,\tau\right) \quad (8.6)$$

- The conditional probability plays an important role in non-equilibrium statistical mechanics. It is used in the expression for the correlation function for property A whose change in time is described as a stationary Markov process:

$$K(\tau=\Delta t)=\int\cdots\int dp_0 dq_0 dp_1 dq_1 W_2(p_1,q_1;p_0,q_0,\tau)A(p_0,q_0)A(p_1,q_1)$$
$$=\int\cdots\int dp_0 dq_0 dp_1 dq_1 W_1(p_0,q_0)P_2(p_1,q_1|p_0,q_0,\tau)A(p_0,q_0)A(p_1,q_1) \qquad (8.7)$$

D. How to Obtain Conditional Probabilities: Master Equations

- Conditional probabilities are calculated using differential equations called master equations. Master equations may be thought of as rate equations and they utilize transition rate probabilities. Example: $w_{j\to l}d\tau\, dl = w_{jl}d\tau\, dl$ is the probability that in a short period of length dt, a transition is made j to l+dl. As such w_{jl} is a transition rate probability. A pleasant feature of master equations is that their derivation and use is pretty clear to a chemist.
- To obtain the master equation we need a mathematical relationship called Markov's Integral Equation, also called the Chapman-Kolmogorov (CK) Equation:

$$P_2(x_2,t_2|x_0,t_0)=\int P_2(x_1,t_1|x_0,t_0)P_2(x_2,t_2|x_1,t_1)dx_1$$
$$=\int P_2(x_1|x_0,t_1-t_0)P_2(x_2|x_1,t_2-t_1)dx_1 \qquad (8.8)$$
$$=\int P_2(x_1|x_0,t)P_2(x_2|x_1,\tau)dx_1=P_2(x_2|x_0,t+\tau)$$

where the second and third steps assume the process is Markovian and stationary. We there fore define $\tau=t_2-t_1$ and $t=t_1-t_0$

- Equation 8.8 has the discrete form:

$$P_2(l|l_0;t+\tau)=\sum_j P_2(j|l_0;t)P_2(l|j;\tau) \qquad (8.9)$$

- We also need to take note of two important properties possessed by conditional probabilities:
  - The system or property A has to make a transition to some other state in a time t_2-t_1 =τ: $\int P(l|j,\tau)dl=1$. For discrete states this can be written as $\sum_l P(l|j,\tau)=1$
  - The system or property cannot change instantaneously: $P(l|j,\tau=0)=\delta_{jl}$

Note for convenience we dropped the subscript 2, because it is understood that from now on we deal with stationary Markov processes.

- Three steps to setting up a master equation…

- Because a system cannot change instantaneously
  $P(l|j,\tau) \rightarrow 0 \; as \; \tau \rightarrow 0. \quad \therefore P(l|j,\tau) \approx \tau w_{j\rightarrow l}$ (8.10a)
  and $P(l|l,\tau) \rightarrow 1 \; as \; \tau \rightarrow 0. \quad \therefore P(l|l,\tau) \approx 1-\tau\sum_{k\neq l} w_{l\rightarrow k}$ (8.10b)
- Combine these two equations: $P(l|j;\tau) = \tau w_{j\rightarrow l} + \delta_{lj}\left(1-\tau\sum_{k} w_{l\rightarrow k}\right)$ (8.10c)

- We take (8.10c) and put it into the discrete for of the C-K equation to obtain

$$\frac{P(l|l_0;t+\tau)-P(l|l_0;t)}{\tau} = \sum_j \left[w_{j\rightarrow l} P(j|l_0;t) - w_{l\rightarrow j} P(l|l_0;t) \right] \qquad (8.11)$$

- (6.11) can be written as a differential equation in the limit $\tau \rightarrow 0$

$$\underset{\tau\rightarrow 0}{Lim} \frac{P(l|l_0;t+\tau)-P(l|l_0;t)}{\tau} = \frac{\partial P(l|l_0;t)}{\partial t} = \sum_j \left[w_{j\rightarrow l} P(j|l_0;t) - w_{l\rightarrow j} P(l|l_0;t) \right] \qquad (8.12)$$

which in continuous form is: $\frac{\partial P(l|l_0;t)}{\partial t} = \int_{-\infty}^{+\infty} \left[w_{j\rightarrow l} P(j|l_0;t) - w_{l\rightarrow j} P(l|l_0;t) \right] dj$