PHY 770 -- Statistical Mechanics
11 AM-12:15 PM & 12:30-1:45 PM TR Olin 107

Instructor: Natalie Holzwarth (Olin 300)
Course Webpage: http://www.wfu.edu/~natalie/s14phy770

Lecture 7 & 8 -- Appendix A & Chapter 2
Introduction to Probability and Its Role in Statistical Physics

1. **Probability distribution functions**
2. **Central limit theorem**
3. **Liouville theorem and its quantum equivalent**
4. **Relationship between entropy and notions from probability theory**

PHY 770 Statistical Mechanics

TR 12:30-1:45 PM | OPL 107 | http://www.wfu.edu/~natalie/s14phy770/

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Course schedule for Spring 2014

(Preliminary schedule -- subject to frequent adjustment.) Please note that makeup lectures (indicated in red) are scheduled for Tuesdays or Thursdays at 11 AM - 12:15 PM in Olin 107.

	Lecture date	Text Reading	Topic	Assign.	Due date
1	Tue: 01/14/2014	Chap. 3	Review of macroscopic thermodynamics	#1	02/04/2014
2	Thu: 01/16/2014	Chap. 3	Review of macroscopic thermodynamics	#2	02/04/2014
3	Tue: 01/21/2014	Chap. 3	Thermodynamic potentials	#3	02/04/2014
4	Tue: 01/21/2014	Chap. 3	Thermodynamic stability	#4	02/04/2014
5	Thu: 01/23/2014	Chap. 3	Thermodynamic stability	#5	02/04/2014
	Tue: 01/28/2014		NAWH out of town - no class		
	Thu: 01/30/2014		NAWH out of town - no class		
6	Tue: 02/04/2014	Chap. 4	Phase transitions	#6	02/11/2014
7	Thur: 02/06/2014	Chap. 2	Microscopic analysis of entropy	#7	02/11/2014
8	Thur: 02/06/2014	Chap. 2	Microscopic analysis of entropy	#8	02/11/2014

Some ideas from probability theory

Notation --

Random variable: X

Possible value of X: x

Probability of outcome x: $P_X(x)$

Properties of probability function

Discrete case; $x \Rightarrow x_i \quad i = 1,2,....N$

$$P_X(x_i) \geq 0$$

$$\sum_{i=1}^{N} P_X(x_i) = 1$$

Some ideas from probability theory -- continued

Average value : $\langle X \rangle \equiv \sum_{i=1}^{N} x_i P_X(x_i)$

Moment value : $\langle X^n \rangle \equiv \sum_{i=1}^{N} x_i^{\,n} P_X(x_i)$

Standard diviation : $\sigma_X = \sqrt{\langle X^2 \rangle - \langle X^1 \rangle^2}$

For a continuous variable x where $-\infty \le x \le \infty$:

$$P_X(x) \ge 0$$

$$\int_{-\infty}^{\infty} P_X(x)dx = 1$$

$$\langle X^n \rangle = \int_{-\infty}^{\infty} x^n P_X(x)dx$$

Some ideas from probability theory -- continued

Clever use of Fourier transfroms; the characteristic function :

$$\phi_X(k) \equiv \langle e^{ikx} \rangle = \int_{-\infty}^{\infty} e^{ikx} P_X(x)dx = \sum_{n=1}^{\infty} \frac{(ik)^n \langle X^n \rangle}{n!}$$

Note that, using the inverse Fourier transform :

$$P_X(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikx} \phi_X(k)dk$$

Other useful relationships :

$$\langle X^n \rangle = \frac{1}{i^n} \lim_{k\to 0} \frac{d^n \phi_X(k)}{dk^n}$$

Cummulants : $C_n(X)$

$$\phi_X(k) = \exp\left(\sum_{n=1}^{\infty} \frac{(ik)^n}{n!} C_n(X) \right)$$

$$C_1(X) = \langle X \rangle \qquad C_2(X) = \langle X^2 \rangle - \langle X \rangle^2$$

$$C_3(X) = \langle X^3 \rangle - 3\langle X^2 \rangle \langle X \rangle + 2\langle X \rangle^3$$

Some ideas from probability theory -- continued

Example :

$$P_X(x) = \begin{cases} \frac{2}{\pi}\sqrt{1-x^2} & \text{for } |x| \le 1 \\ 0 & \text{otherwise} \end{cases}$$

$$\phi_X(k) \equiv \langle e^{ikx} \rangle = \int_{-\infty}^{\infty} e^{ikx} P_X(x)dx = \frac{2}{\pi}\int_{-1}^{1} e^{ikx}\sqrt{1-x^2}\,dx = \frac{2}{k} J_1(k)$$

Using the assending series expansion :

$$\phi_X(k) = \frac{2}{k} J_1(k) = 1 - \frac{1}{4}\frac{k^2}{2!} + \frac{1}{8}\frac{k^4}{4!}$$

From : $\phi_X(k) \equiv \langle e^{ikx} \rangle = \int_{-\infty}^{\infty} e^{ikx} P_X(x)dx = \sum_{n=1}^{\infty} \frac{(ik)^n \langle X^n \rangle}{n!}$

$$\langle X \rangle = \langle X^3 \rangle = \langle X^5 \rangle = ... = 0$$

$$\langle X^2 \rangle = \frac{1}{4} \qquad \langle X^4 \rangle = \frac{1}{8}$$

Some ideas from probability theory – continued

Example: Consider a random walk in one dimension for which the walker at each step is equally likely to take a step with displacement anywhere in the interval

$d-a \le x \le d+a \qquad (a<d)$.

Each step is independent of the others. After N steps, the displacement of the walker is

$S=X_1+X_2+\dots X_N$

What is the average $\langle S \rangle$ and standard deviation σ_S?

$$P_X(x) = \begin{cases} \frac{1}{2a} & \text{for } d-a \le x \le d+a \\ 0 & \text{otherwise} \end{cases}$$

$$\text{For a single step : } \quad \phi_X(k) \equiv \langle e^{ikx} \rangle = \int_{-\infty}^{\infty} e^{ikx} P_X(x) dx = \frac{1}{2a} \int_{d-a}^{d+a} e^{ikx} dx = e^{ikd} \frac{\sin(ka)}{ka}$$

Some ideas from probability theory – continued

Characteristic function for a single step :

$$\phi_X(k) \equiv \langle e^{ikx} \rangle = e^{ikd} \frac{\sin(ka)}{ka}$$

Characteristic function for S (N steps) :

$$\phi_S(k) = (\phi_X(k))^N = \left(e^{ikd} \frac{\sin(ka)}{ka} \right)^N$$

Expansion in powers of k :

$$\phi_S(k) = \left(e^{ikd} \frac{\sin(ka)}{ka} \right)^N = 1 + (iNd)k - \left(\frac{1}{6} Na^2 + \frac{1}{2} N^2 d^2 \right) k^2 + \dots$$

$$\Rightarrow \langle S \rangle = Nd \qquad \langle S^2 \rangle = \frac{1}{3} Na^2 + N^2 d^2$$

$$\sigma_S = \sqrt{\langle S^2 \rangle - \langle S \rangle^2} = \sqrt{\frac{N}{3}} a$$

Some ideas from probability theory – continued

Typical probability functions

- ❑ Binomial distribution
- ❑ Gaussian distribution
- ❑ Poisson distribution

❑ Binomial distribution

Consider a process with 2 outcomes:

0 with probability p

1 with probability $q=1-p$

For N “trials” of the process, n_0 denotes the number outcomes 0 and n_1 denotes the number of outcomes 1, with $N=n_0+n_1$.

$$P_N(n_1) = \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{(N-n_1)}$$

Binomial distribution continued:

$$P_N(n_1) = \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{(N-n_1)}$$

Note that :

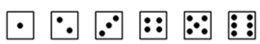
$$\sum_{n_1=0}^{N} P_N(n_1) = \sum_{n_1=0}^{N} \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{(N-n_1)} = (p+q)^N = 1$$

Can show that :

$$\langle n_1 \rangle = Np$$

$$\langle n_1^2 \rangle = (Np)^2 + Npq$$

$$\sigma_N = \sqrt{Npq}$$

Example: Dice throws 

On average, how many times must a die be thrown until "4" appears?

Let p = probability of getting 4 on one throw ($p = 1/6$)

Let q = probability of not getting 4 on one throw

Probability of first getting 4 on nth throw : $P_n = pq^{n-1}$

Mean # of throws : $m = \sum_{n=1}^{\infty} npq^{n-1} = p\frac{d}{dq}\sum_{n=0}^{\infty} q^n$

$$= p\frac{d}{dq}\frac{1}{1\text{-}q} = p\frac{1}{(1-q)^2} = \frac{1}{p}$$

Gaussian distribution

Consider the binomial distribution in the limit of large *N* and large *pN*:

$$P_N(n) = \frac{N!}{n!(N-n)!} p^n q^{(N-n)}$$

$$\langle n \rangle = Np$$

Stirling approximation : $n! \approx \sqrt{2\pi n}\left(\frac{n}{e}\right)^n$

$$P_N(n) \approx P_N(\langle n \rangle)\exp\left(-\frac{(n-\langle n \rangle)^2}{2Npq}\right) \to \frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{(n-\langle n \rangle)^2}{2\sigma^2}\right)$$

Poisson distribution

Consider the binomial distribution in the limit of large *N* and *pN =a<< N*:

$$P_N(n)=\frac{N!}{n!(N-n)!}p^n q^{(N-n)}$$
$$\langle n\rangle = Np \equiv a$$
$$P_N(n)\approx \frac{a^n e^{-a}}{n!}$$
$$\text{Note that : } \sum_{n=0}^{\infty}\frac{a^n e^{-a}}{n!} = e^a e^{-a} = 1$$

Poisson distribution example

Consider a monolayer thin sheet of gold foil as a target for neutron scattering. Assume that the probability that in any given pulse of the beam the probability that the beam will scatter from the gold nuclei is given by the Poisson distribution with a=2. Determine the probability that n=0 and that n=2.

$$P_{Poisson}(n)=\frac{a^n e^{-a}}{n!}$$
$$P_{Poisson}(0)=2^0 e^{-2}=0.135$$
$$P_{Poisson}(1)=\frac{2^1 e^{-2}}{1}=0.271$$
$$P_{Poisson}(2)=\frac{2^2 e^{-2}}{2}=0.271$$
$$P_{Poisson}(3)=\frac{2^3 e^{-2}}{3!}=0.180$$
$$P_{Poisson}(4)=\frac{2^4 e^{-2}}{4!}=0.090$$

Central limit theorem

Consider *N* independent stochastic variables X_i, *i=1,2,..N.* What is the distribution of their sum

$Y_N=(X_1+...X_N)/N$

Characteristic function for Y_N :

$$\phi_Y(k)=\int_{-\infty}^{\infty}dx_1....\int_{-\infty}^{\infty}dx_N e^{ik(x_1+x_2+...x_N)/N}P_{X_1}(x_1)...P_{X_N}(x_N)$$
$$=(\phi_X(k/N))^N$$
$$\approx\left(1-\frac{1}{2}\frac{k^2\sigma_X^2}{N^2}+...\right)^N \underset{N\to\infty}{\approx} \exp\left(-\frac{k^2\sigma_X^2}{2N}\right)$$
$$P_Y(y)\approx\frac{1}{2\pi}\int_{-\infty}^{\infty}dk\, e^{-iky}\exp\left(-\frac{k^2\sigma_X^2}{2N}\right)=\sqrt{\frac{N}{2\pi\sigma_X^2}}\exp\left(-\frac{Ny^2}{2\sigma_X^2}\right)$$

Central limit theorem

Consider N independent stochastic variables X_i, $i=1,2,..N$.

What is the distribution of their sum

$Y_N=(X_1+\ldots X_N)/N$

$$P_Y(y)=\sqrt{\frac{1}{2\pi\sigma_X^2/N}}\exp\left(-\frac{y^2}{2\sigma_X^2/N}\right)$$

→Distribution function for Y is a Gaussian distribution centered at <x> and with variance $\sigma_X/\sqrt{N}$

Justification of statistical treatment of macroscopic systems

Classical mechanics argument ant the Liouville theorem

Liouville's theorem:

Imagine a collection of particles obeying the Canonical equations of motion in phase space.

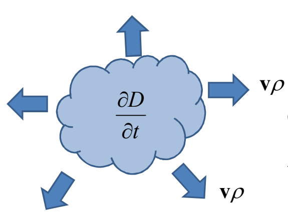
Let D denote the "distribution" of particles in phase space:

$$D=D(\{q_1\cdots q_{3N}\},\{p_1\cdots p_{3N}\},t)$$

Liouville's theorm shows that:

$$\frac{dD}{dt}=0 \qquad \Rightarrow D \text{ is constant in time}$$

Proof of Liouville'e theorem:



Continuity equation:

$$\frac{\partial D}{\partial t}=-\nabla\cdot(\mathbf{v}D)$$

Note: in this case, the velocity is the $6N$ dimensional vector:

$$\mathbf{v}=(\dot{\mathbf{r}}_1,\dot{\mathbf{r}}_2,\ldots\dot{\mathbf{r}}_N,\dot{\mathbf{p}}_1,\dot{\mathbf{p}}_2,\ldots\dot{\mathbf{p}}_N)$$

We also have a $6N$ dimensional gradient:

$$\nabla=(\nabla_{\mathbf{r}_1},\nabla_{\mathbf{r}_2},\ldots\nabla_{\mathbf{r}_N},\nabla_{\mathbf{p}_1},\nabla_{\mathbf{p}_2},\ldots\nabla_{\mathbf{p}_N})$$

$$\frac{\partial D}{\partial t} = -\nabla \cdot (\mathbf{v}D)$$

$$= -\sum_{j=1}^{3N}\left[\frac{\partial}{\partial q_j}(\dot{q}_j D) + \frac{\partial}{\partial p_j}(\dot{p}_j D)\right]$$

$$= -\sum_{j=1}^{3N}\left[\frac{\partial D}{\partial q_j}\dot{q}_j + \frac{\partial D}{\partial p_j}\dot{p}_j\right] - D\sum_{j=1}^{3N}\left[\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j}\right]$$

$$\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} = \frac{\partial^2 H}{\partial q_j \partial p_j} + \left(-\frac{\partial^2 H}{\partial p_j \partial q_j}\right) = 0$$

0

$$\frac{\partial D}{\partial t} = -\sum_{j=1}^{3N}\left[\frac{\partial D}{\partial q_j}\dot{q}_j + \frac{\partial D}{\partial p_j}\dot{p}_j\right] - D\sum_{j=1}^{3N}\left[\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j}\right]$$

$$\frac{\partial D}{\partial t} = -\sum_{j=1}^{3N}\left[\frac{\partial D}{\partial q_j}\dot{q}_j + \frac{\partial D}{\partial p_j}\dot{p}_j\right]$$

$$\Rightarrow \frac{\partial D}{\partial t} + \sum_{j=1}^{3N}\left[\frac{\partial D}{\partial q_j}\dot{q}_j + \frac{\partial D}{\partial p_j}\dot{p}_j\right] = \frac{dD}{dt} = 0$$

Complexity and entropy

Microscopic definition of entropy

$$S(N,E,n) = k_B \ln\left(\mathcal{N}_N(E,n)\right)$$

In this case, we have *N* particles having a total energy *E* and a macroscopic parameter *n*.

$\mathcal{N}_N(E,n)$ denotes the multiplicity of microscopic states having the same parameters. Each of these states are assumed to equally likely to occur.

Example:

Suppose you have N spin-1/2 particles. How many microscopic states does the system have?

For $N=10$: ↑↓ ↑↑↓ ↓↓↑↓↑ total = $2^{10}=1024$

For N=100 total= $2^{100}=10^{30}$

Now, consider N spin-1/2 particles with n ↑.

$$\mathcal{N}_N(n) = \frac{N!}{n!(N-n)!}$$

Spin-1/2 system continued

Recall the binomial distribution : for fixed a and b

$$(a+b)^N = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} a^{N-n} b^n$$

$$\Rightarrow \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} = (1+1)^N = 2^N$$

Fraction of microscopic states for this systerm?

$$\mathcal{F}_N(n) = \frac{1}{2^N}\mathcal{N}_N(n) = \frac{1}{2^N}\frac{N!}{n!(N-n)!} = \frac{N!}{n!(N-n)!}\left(\frac{1}{2}\right)^n\left(\frac{1}{2}\right)^{N-n}$$

Spin-1/2 system continued

Fraction of microscopic states for this systerm?

$$\mathcal{F}_N(n) = \frac{1}{2^N}\mathcal{N}_N(n) = \frac{1}{2^N}\frac{N!}{n!(N-n)!} = \frac{N!}{n!(N-n)!}\left(\frac{1}{2}\right)^n\left(\frac{1}{2}\right)^{N-n}$$

For $N \rightarrow \infty$

$$\mathcal{F}_N(n) \approx \frac{1}{\sqrt{2\pi\sigma_N}} \exp\left(-\frac{(n-\langle n\rangle)^2}{2\sigma_N^{\ 2}}\right)$$

where $\langle n\rangle = N/2$ and $\sigma_N = \sqrt{N}/2$

Spin-1/2 system continued

Entropy for this system :

$$\mathcal{N}_N(n) = \frac{N!}{n!(N-n)!}$$

$$S(N,n) = k_B \ln(\mathcal{N}_N(n)) = k_B \ln\left(\frac{N!}{n!(N-n)!}\right)$$

Stirling approximation : $N! \approx \sqrt{2\pi N} N^N e^{-N}$

$$\ln(N!) \approx N\ln(N) - N$$

$$S(N,n) = k_B \ln(\mathcal{N}_N(n)) \approx k_B \ln\left(\frac{N^N}{n^n (N-n)^{N-n}}\right)$$

2/6/2014 PHY 770 Spring 2014 -- Lectures 7 & 8 25

Spin-1/2 system continued

$$S(N,n) = k_B \ln(\mathcal{N}_N(n)) = k_B \ln\left(\frac{N!}{n!(N-n)!}\right)$$

$$S(N,n) = k_B \ln(\mathcal{N}_N(n)) \approx k_B \ln\left(\frac{N^N}{n^n (N-n)^{N-n}}\right)$$

$$S(N,\langle n\rangle) \approx k_B \ln\left(\frac{N^N}{\langle n\rangle^{\langle n\rangle} (N-\langle n\rangle)^{N-\langle n\rangle}}\right) = Nk_B \ln(2)$$

2/6/2014 PHY 770 Spring 2014 -- Lectures 7 & 8 26

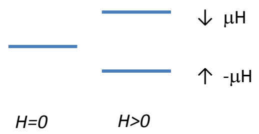
Relationship between probability function and entropy

Fraction of microscopic states for systerm

$$\mathcal{F}_N(n) = P_N(n) = \frac{1}{\mathcal{N}_N} \mathcal{N}_N(n) = \frac{1}{\mathcal{N}_N} \exp(S(N,n)/k_B)$$

2/6/2014 PHY 770 Spring 2014 -- Lectures 7 & 8 27

Spin-1/2 system continued – effects of Magnetic field



$$\langle E \rangle = -\mu \langle n \rangle H + \mu (N - \langle n \rangle) H = \mu N H - 2\mu \langle n \rangle H$$

$$\text{Note that: } \langle n \rangle = \frac{N}{2} - \frac{\langle E \rangle}{2\mu H}$$

Spin-1/2 system continued – effects of Magnetic field -- continued

Approximate entropy for this case (fixed $\langle E \rangle, H$);

Stirling approximation:

$$S(N, \langle E \rangle, H) \approx k_B N \ln N - k_B \left(\frac{N}{2} - \frac{\langle E \rangle}{2\mu H} \right) \ln \left(\frac{N}{2} - \frac{\langle E \rangle}{2\mu H} \right) - k_B \left(\frac{N}{2} + \frac{\langle E \rangle}{2\mu H} \right) \ln \left(\frac{N}{2} + \frac{\langle E \rangle}{2\mu H} \right)$$

Spin-1/2 system continued – effects of Magnetic field -- continued

Big leap:

Assume the microscopic entropy function **IS** the same as the macroscopic entropy found in classical thermodynamics $\left(\frac{\partial S}{\partial E} \right)_{H,N} = \frac{1}{T}$

$$S(N, \langle E \rangle, H) \approx k_B N \ln N - k_B \left(\frac{N}{2} - \frac{\langle E \rangle}{2\mu H} \right) \ln \left(\frac{N}{2} - \frac{\langle E \rangle}{2\mu H} \right) - k_B \left(\frac{N}{2} + \frac{\langle E \rangle}{2\mu H} \right) \ln \left(\frac{N}{2} + \frac{\langle E \rangle}{2\mu H} \right)$$

$$\left(\frac{\partial S}{\partial E} \right)_{H,N} = \frac{1}{T} = \frac{k_B}{2\mu H} \ln \left(\frac{N - \frac{\langle E \rangle}{2\mu H}}{N + \frac{\langle E \rangle}{2\mu H}} \right)$$