PHY 770 -- Statistical Mechanics
12:30-1:45 PM TR Olin 107

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

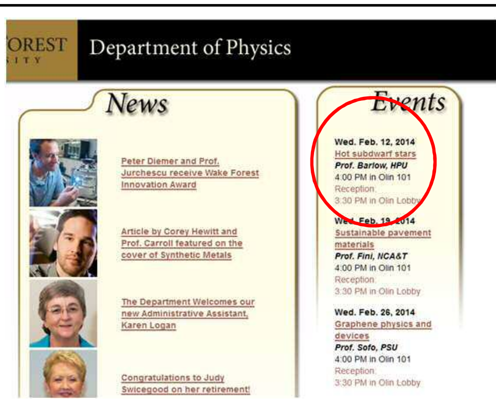
Lecture 9 -- Chapter 2
Boltzmann's Entropy

1. Microscopic analyses of entropy
   - Spin system
   - Einstein solid
   - Ideal gas

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
9	Tue: 02/11/2014	Chap. 2	Microscopic analysis of entropy	#9	02/18/2014
10	Thur: 02/13/2014	Chap. 5	Equilibrium Statistical Mechanics	#10	02/18/2014



WFU Physics Colloquium

TITLE: The Coolest Little Hot Stars You've Never Heard Of

SPEAKER: Brad N. Barlow,

Department of Physics
High Point University

TIME: Wednesday February 12, 2014 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

The enigmatic hot subdwarf stars represent one of the least-understood stages of stellar evolution. Theory shows they likely formed from red giants that lost their outer hydrogen envelopes due to Roche lobe overflow and common envelope interactions with a nearby companion star. Observations support this idea as the large majority of hot subdwarfs are, in fact, in binaries. Although binary population synthesis models are generally successful at forming hot subdwarf systems, these models are relatively unconstrained and fail at predicting their orbital periods and companion masses. Here I will (i) give a brief introduction to hot subdwarf stars, (ii) describe three main techniques we use to detect binaries with varying companion masses, and (iii) discuss new systems we found that are

Some comments on previous topics:
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:

$$\phi_Y(k)=\int_{-\infty}^{\infty}dx_1....\int_{-\infty}^{\infty}dx_N e^{ik(x_1+x_2+...x_N)/N}P_{X_1}(x_1)...P_{X_N}(x_N)$$

$$=(\phi_X(k/N))^N$$

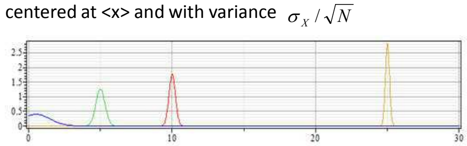
$$\approx\left(1-\frac{1}{2}\frac{k^2\sigma_X^2}{N^2}+...\right)^N \underset{N\to\infty}{\approx} \exp\left(-\frac{k^2\sigma_X^2}{2N}\right)$$

$$P_Y(y)\approx\frac{1}{2\pi}\int_{-\infty}^{\infty}dk\, e^{-iky}\exp\left(-\frac{k^2\sigma_X^2}{2N}\right)=\sqrt{\frac{N}{2\pi\sigma_X^2}}\exp\left(-\frac{Ny^2}{2\sigma_X^2}\right)$$

Central limit theorem
Consider N independent stochastic variables X_i, $i=1,2,..N$.
What is the distribution of their sum
$Y_N=(X_1+...X_N)/N$

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

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



Microscopic definition of entropy – due to Boltzmann

Consider a system with *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.

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

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* ↑ (all with the same energy).

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

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

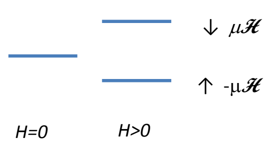
$$\ln(N!) \approx N\ln(N) - N$$

$$S(N,n) = k_B \ln(\mathcal{N}_N(n)) \approx k_B N(\ln N - 1)$$

$$- k_B n(\ln n - 1) - k_B (N-n)(\ln(N-n) - 1)$$

$$= k_B (N \ln N - n \ln n - (N-n)\ln(N-n))$$

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



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

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

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

Previous result :

$$S(N,\langle n\rangle)\approx k_B\left(N\ln N-\langle n\rangle\ln\langle n\rangle-(N-\langle n\rangle)\ln(N-\langle n\rangle)\right)$$

Expression in terms of $\langle E\rangle,\boldsymbol{\mathcal{H}}$:

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

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

Big leap:

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

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

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

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

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

Solving for $\langle E\rangle$ versus T relationsh ip

$$\langle E\rangle\Rightarrow U(T,N,\boldsymbol{\mathcal{H}})=N\mu\boldsymbol{\mathcal{H}}\tanh\left(\frac{\mu\boldsymbol{\mathcal{H}}}{k_BT}\right)$$

Heat capacity :

$$C_{N,\boldsymbol{\mathcal{H}}}=\left(\frac{\partial U}{\partial T}\right)_{N,\boldsymbol{\mathcal{H}}}=Nk_B\left(\frac{\mu\boldsymbol{\mathcal{H}}}{k_BT}\right)^2\frac{1}{\cosh^2\left(\frac{\mu\boldsymbol{\mathcal{H}}}{k_BT}\right)}$$

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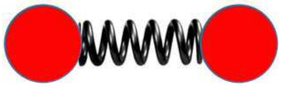
Example: Einstein solid – simple model of vibrational modes



Energy for each oscillator : $\varepsilon_i = \hbar\omega\left(n_i + \frac{1}{2}\right) \quad n_i = 0,1,..\infty$

Energy for N oscillators : $E(N,q) = \hbar\omega\left(\frac{N}{2} + q\right) \quad q = 0,1,..\infty$

here q comes from combinations of $\{n_i\}$ for N oscillators

Note : N is a multiple of 3 for a 3-dimensional system

Einstein solid – continued

Energy for N oscillators : $E(N,q) = \hbar\omega\left(\frac{N}{2} + q\right) \quad q = 0,1,..\infty$

Multiplicity of $E(N,q)$:

Count ways of distributing q quanta over N oscillators :

Example for *q*=3 and *N*=2

N(1)	*N(2)*	
q=3	q=0	(xxx|)
q=2	q=1	(xx|x)
q=1	q=2	(x|xx)
q=0	q=3	(|xxx)

$$\mathcal{N}_N(q) = \frac{(N-1+q)!}{q!(N-1)!}$$

Einstein solid – continued

Energy for N oscillators : $E(N,q) = \hbar\omega\left(\frac{N}{2} + q\right) \quad q = 0,1,..\infty$

$$\mathcal{N}_N(q) = \frac{(N-1+q)!}{q!(N-1)!}$$

$$S(N,q) = k_B \ln(\mathcal{N}_N(q)) = k_B \ln\left(\frac{(N-1+q)!}{q!(N-1)!}\right)$$

$$\approx k_B\left((N-1+q)\ln(N-1+q) - q\ln q - (N-1)\ln(N-1)\right)$$

$$q = \frac{E}{\hbar\omega} - \frac{N}{2}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{\hbar\omega}\left(\frac{\partial S}{\partial q}\right)_N = \frac{k_B}{\hbar\omega}\left(\ln\left(\frac{N-1+q}{q}\right)\right)$$

Einstein solid – continued

$$\text{Energy for } N \text{ oscillators: } E(N,q) = \hbar\omega\left(\frac{N}{2}+q\right) \quad q = 0,1,..\infty$$

$$\frac{1}{T} = \frac{k_B}{\hbar\omega}\left(\ln\left(\frac{N-1+q}{q}\right)\right) = \frac{k_B}{\hbar\omega}\left(\ln\left(\frac{\frac{E}{\hbar\omega}+\frac{N}{2}-1}{\frac{E}{\hbar\omega}-\frac{N}{2}}\right)\right)$$

$$\approx \frac{k_B}{\hbar\omega}\left(\ln\left(\frac{\frac{E}{\hbar\omega}+\frac{N}{2}}{\frac{E}{\hbar\omega}-\frac{N}{2}}\right)\right)$$

$$\text{Solving for } E \Rightarrow U(T,N) = N\hbar\omega\left(\frac{1}{2}+\frac{1}{e^{\hbar\omega/k_BT}-1}\right)$$

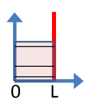
$$\text{Heat capacity: } C_N = \left(\frac{\partial U}{\partial T}\right)_N = \frac{N(\hbar\omega)^2 e^{\hbar\omega/k_BT}}{k_BT^2\left(e^{\hbar\omega/k_BT}-1\right)^2}$$

Example: Ideal gas in *d* dimensions:
Relationship between classical and quantum microstate analyses:

Classical	Quantum
$\frac{1}{N!h^{dN}}\int d^{dN}r\ d^{dN}p \Rightarrow$	$\sum_n$

Example for quantum particle in 1-dimensional box:

Classical	Quantum
$\frac{p_x^2}{2m} \le E$	$\varepsilon_n = \frac{h^2n^2}{8mL^2} \le E$



Example: single particle of mass m confined within a 1 dimensional box of length L; d=1, N=1:

Classical treatment :

$0 \le x \le L$:

$-\sqrt{2mE} \le p_x \le \sqrt{2mE}$

$$\mathcal{N}_{Cl}(E) = \int_0^L dx \int_{-\sqrt{2mE}}^{\sqrt{2mE}} dp_x = 2L\sqrt{2mE}$$

Quantum treatment :

$$\text{Discrete energies : } \varepsilon_n = \frac{h^2n^2}{8mL^2} \quad n = 1,2,3\cdots$$

$$\mathcal{N}_Q(E) = \sum_{n=1}^{\varepsilon_n \le E} = \frac{2L}{h}\sqrt{2mE}$$

Classical analysis for $\mathcal{N}$(E) for d=1, N=2

Classical treatment :

$$0 \le x_1 \le L \qquad 0 \le x_2 \le L$$

$$0 \le p_{x,1}^2 + p_{x,2}^2 \le 2mE$$

$$\mathcal{N}_{Cl}(E) = \int_0^L dx_1 \int_0^L dx_2 \iint_{0 \le p_{x,1}^2 + p_{x,2}^2 \le 2mE} dp_{x,1} dp_{x,2}$$

Trick: Map problem into general problem of finding volume of ν dimensional hypersphere of radius R

$$V_\nu(R) \equiv \iiint_{x_1^2+x_2^2+\cdots x_\nu^2 \le R^2} dx_1 dx_2 dx_3 dx_4 \cdots dx_\nu = C_\nu R^\nu = \nu C_\nu \int_0^R r^{\nu-1} dr \quad \text{where } R = \sqrt{2mE}$$

Note that : $V_1(R) = \int_{-R}^{R} dx_1 = 2R$

$$V_2(R) = 2\pi \int_0^R r\,dr = \pi R^2$$

$$V_3(R) = 4\pi \int_0^R r^2 dr = \frac{4\pi}{3} R^3$$

Clever trick to find C_ν:

Note that : $I_\nu \equiv \left(\int_{-\infty}^{\infty} dx\, e^{-x^2} \right)^\nu = \pi^{\frac{\nu}{2}}$

This can be written in the form :

$$I_\nu = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \cdots \int_{-\infty}^{\infty} dx_\nu\, e^{-x_1^2 - x_2^2 - \cdots - x_\nu^2} = \nu C_\nu \int_0^\infty r^{\nu-1} e^{-r^2} dr$$

$$I_\nu = \pi^{\frac{\nu}{2}} = \nu C_\nu \int_0^\infty r^{\nu-1} e^{-r^2} dr$$

Gamma function : $\Gamma(\alpha) \equiv \int_0^\infty dt\, t^{\alpha-1} e^{-t}$

$$\Rightarrow \int_0^\infty r^{\nu-1} e^{-r^2} dr = \frac{1}{2}\Gamma\left(\tfrac{\nu}{2}\right)$$

$$\nu C_\nu \frac{1}{2}\Gamma\left(\tfrac{\nu}{2}\right) = \pi^{\frac{\nu}{2}}$$

$$\Rightarrow C_\nu = \frac{2\pi^{\frac{\nu}{2}}}{\nu\Gamma\left(\frac{\nu}{2}\right)} = \frac{\pi^{\frac{\nu}{2}}}{\Gamma\left(\frac{\nu}{2}+1\right)}$$

Note : $\alpha\Gamma(\alpha) = \Gamma(\alpha+1)$

ν	Γ(ν/2)	C_ν
1	$\sqrt{\pi}$	2
2	1	π
3	$\frac{1}{2}\sqrt{\pi}$	$\frac{4\pi}{3}$

Result for $\mathcal{N}$(E) for d=1, N=2

$$\mathcal{N}_{Cl}(E) = \int_0^L dx_1 \int_0^L dx_2 \iint_{0 \le p_{x,1}^2 + p_{x,2}^2 \le 2mE} dp_{x,1} dp_{x,2}$$

$$= L^2 \pi (2mE) \quad \text{(same as result for d=2, N=1)}$$

Check :

$$\text{Let } E \equiv \frac{h^2 \kappa^2}{8mL^2} \text{ so that } \frac{1}{h^2} \mathcal{N}_{Cl}(\kappa^2) = \frac{\pi}{4} \kappa^2$$

$$\frac{1}{h^2} \mathcal{N}_{Cl}(\kappa^2) = \frac{\pi}{4} \kappa^2 \qquad \mathcal{N}_Q(\kappa^2) = \sum_{n_1^2 + n_2^2 \le \kappa^2}$$

κ^2	$\mathcal{N}_{Cl}$	$\mathcal{N}_Q$
2	1.571	1.000
5	3.927	3.000
8	6.283	4.000
10	7.854	6.000
13	10.210	8.000
17	13.352	10.000
18	14.137	11.000
20	15.708	13.000
25	19.635	16.000

Microstate count for N particles in d-dimensions

Classical microstate distributi on

$$\mathcal{N}(E) = \frac{1}{N! h^{dN}} \int_{\sum_i \frac{p_i^2}{2m} \le E} d^{dN} r \; d^{dN} p$$

$$= \frac{L^{dN}}{N! h^{dN}} \frac{\pi^{dN/2}}{\Gamma\left(\frac{dN}{2} + 1\right)} (2mE)^{dN/2}$$

$$= \frac{1}{N!} \left(\frac{L}{h}\right)^{dN} \frac{\left((2\pi mE)^{dN/2}\right)}{\Gamma\left(\frac{dN}{2} + 1\right)}$$

For $d = 3,\ L^3 \equiv V$

$$\mathcal{N}(E, V, N) = \frac{1}{N!} \left(\frac{V}{h^3}\right)^N \frac{\left((2\pi mE)^{3N/2}\right)}{\Gamma\left(\frac{3N}{2} + 1\right)}$$

Boltzmann entropy function

$$S(E,V,N) = k_B \ln \mathcal{N}(E,V,N)$$

For 3-dimension system of N independent particles

$$\mathcal{N}(E,V,N) = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \frac{\left((2\pi mE)^{3N/2}\right)}{\Gamma\left(\frac{3N}{2}+1\right)}$$

$$= \frac{V^N}{N!\Gamma\left(\frac{3N}{2}+1\right)}\left(\frac{2\pi mE}{h^2}\right)^{3N/2}$$

Stirling approximation for $x \to \infty$:

$$x! \equiv \Gamma(x+1) \qquad \ln(\Gamma(x+1)) \approx x\ln x - x + \tfrac{1}{2}\ln(2\pi x)$$

To leading order in N:

$$S(E,V,N) = Nk_B\left(\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}\right)$$

Note: more correct analysis would use:

$$S(E,V,N) = k_B \ln \Omega(E,V,N)$$

where $\Omega(E,V,N) = \dfrac{d\mathcal{N}(E,V,N)}{dE}$

$$\mathcal{N}(E,V,N) = \frac{V^N}{N!\Gamma\left(\frac{3N}{2}+1\right)}\left(\frac{2\pi mE}{h^2}\right)^{3N/2}$$

$$\frac{d\mathcal{N}(E,V,N)}{dE} = \mathcal{N}(E,V,N)\frac{3N}{2E}$$

$$\ln\frac{d\mathcal{N}(E,V,N)}{dE} = \ln\mathcal{N}(E,V,N) - \ln\frac{2E}{3N}$$

$$\underset{N\to\infty}{\approx} \ln\mathcal{N}(E,V,N)$$

$$S(E,V,N) = Nk_B\left(\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}\right)$$

Relation to temperature and other thermodynamic variables

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2}Nk_B\frac{1}{E}$$

$$\Rightarrow E = \frac{3}{2}Nk_BT \qquad \text{Recall: } U = \frac{Nk_BT}{\gamma - 1}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = Nk_B\frac{1}{V}$$

$$\Rightarrow PV = Nk_BT$$

Comparison of Boltzmann and macroscopic results

Boltzmann results :

$$S(E,V,N) = Nk\left(\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}\right)$$

Macroscopic ideal gas : $U = \frac{NkT}{\gamma - 1}$

with $\gamma = \frac{5}{3}$ for mono atomic case

$$S_{macroscopic}(T,V,N) = \frac{Nk_B}{\gamma - 1}\ln\left(\frac{TV^{\gamma-1}}{T_0 V_0^{\gamma-1}}\right) + S_0$$

$$S_{macroscopic}(U,V,N) = Nk_B\left(\ln V + \frac{1}{\gamma - 1}\ln\left(\frac{U}{N}\right)\right) + (\text{constants})$$

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