PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 34:

Treatment of particle interactions in statistical mechanics; electron spin effects

Reading: Sections 8.2
(also, part of Section 6.2 concerning spin)

1. **Simple model of magnetism without interactions**
2. **Effects of spin interactions – Heisenberg model**
3. **Effects of spin interactions – Ising model**

28	Fri: 04/09/2021	Chap. 7.3 & 7.4	Bose and Fermi statistics	#23	04/12/2021
29	Mon: 04/12/2021	Chap. 7.3	Fermi examples	#24	04/16/2021
30	Wed: 04/14/2021	Chap. 7.5	Bose examples and lattice vibrations		
31	Fri: 04/16/2021	Chap. 7.6	Bose condensation		
32	Mon: 04/19/2021	Chap. 7.6 & 8.1	Interacting particles	#25	04/21/2021
33	Wed: 04/21/2021	Chap. 8.1	Interacting particles	#26	04/23/2021
34	Fri: 04/23/2021	Chap. 8.2	Spin magnetism		
35	Mon: 04/26/2021	Chap. 8.2	Spin magnetism		
36	Wed: 04/28/2021		Review		
37	Fri: 04/30/2021		Review		
37	Mon: 05/03/2021		Review		
38	Wed: 05/05/2021		Review		

Important dates: Final exams available < May 6; due May 14
Outstanding work due May 14

Comment on homework assignment from Monday's lecture

Based on Lennard-Jones interaction: for parameters r_0 and Φ_0

$$\phi_{pair}(|\mathbf{r}_1 - \mathbf{r}_2|) = \Phi_0 \left(\left(\frac{r_0}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)^{12} - 2 \left(\frac{r_0}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)^{6} \right)$$

$$I_{pair}(\Phi_0 / kT) = \int_0^\infty u^2 du \left(e^{-b\left(u^{-12} - 2u^{-6}\right)} - 1 \right) \quad \text{where } b \equiv \frac{\Phi_0}{kT}$$

For practical calculations we can write

$$I_{pair}(\Phi_0 / kT) = \int_{u_{\min}}^{u_{\max}} u^2 du \left(e^{-b\left(u^{-12} - 2u^{-6}\right)} - 1 \right) \qquad u_{\min} \approx 0.01; \;\; u_{\max} \approx 100$$

Your questions –

From Mike -- I'm assuming the Ising model is only an accurate approximation for ferromagnets. In this case, how do we deal with antiferromagnets?

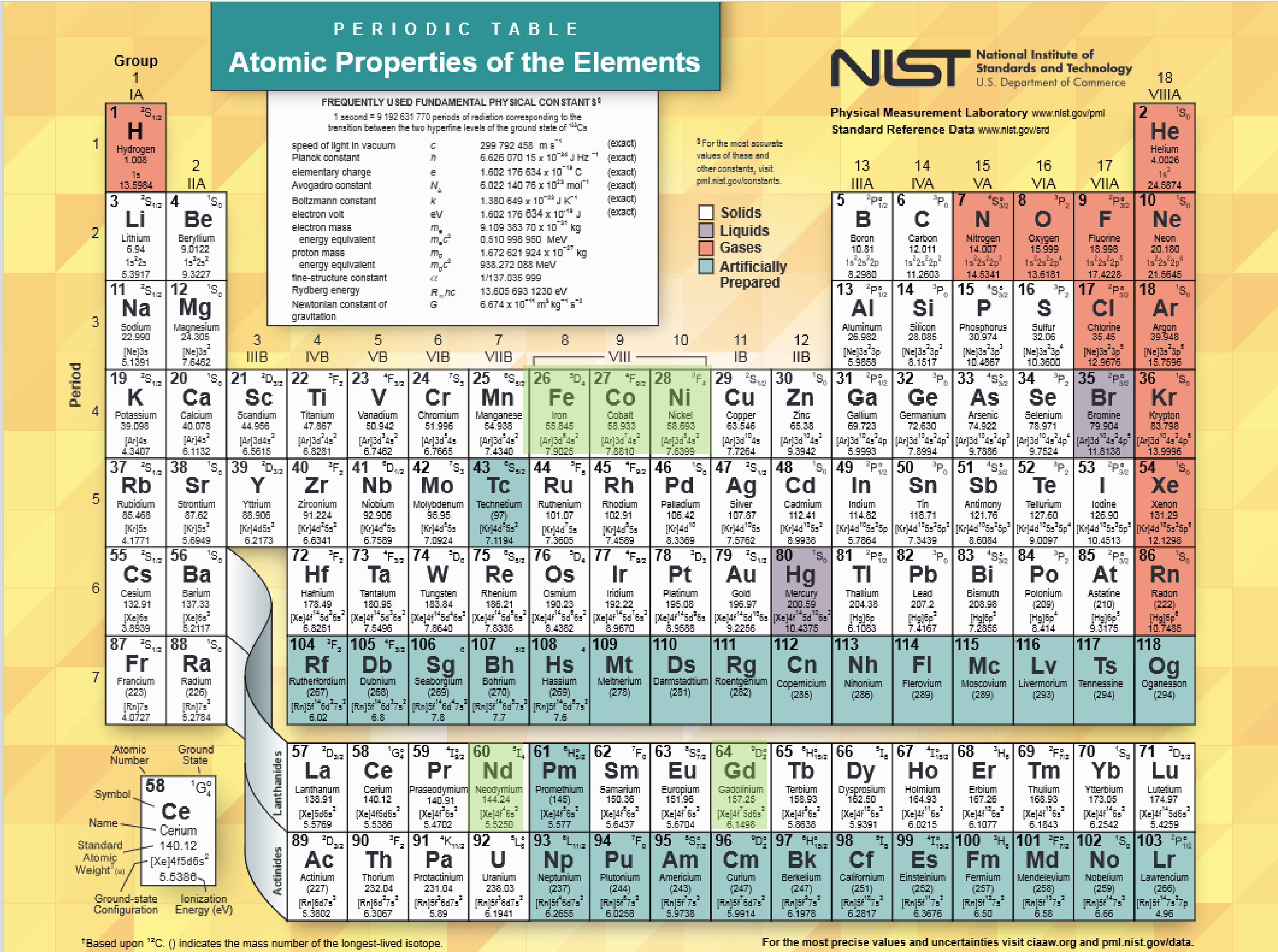
From Kristen -- 1. How is it that the system discussed can become more ordered as the temperature gets higher, doesn't this violate entropy?
2. Could you go over how we get the average expected spin values (equation 8.49) from the partition function, just in this case especially?

Note: Your textbook focuses on the magnetism due to the intrinsic spin of an electron with spin $s=½$. Certainly, the magnetic phenomena are generally traced to that basic physics. However, very interesting magnetic effects are due to atoms which have multiple electrons in localized quantum states which can be well modelled in terms of a total electron spin which we will call S with the knowledge that S can have values larger than ½. Interesting magnetic materials can be described as paramagnetic or ferromagnetic and other more complicated phenomena such as anti ferromagnetic, etc.

Pierre Curie 1859-1906

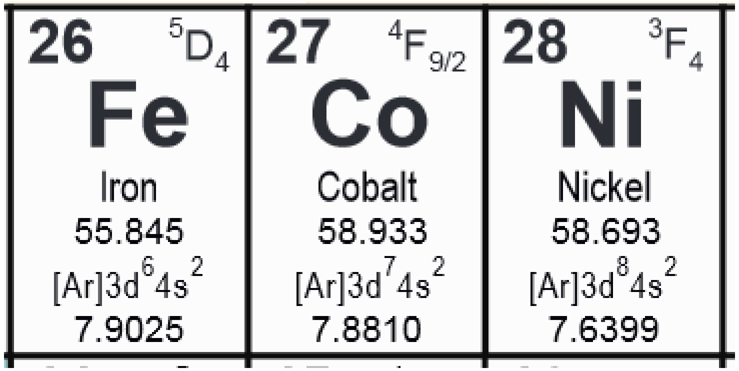
His name is associated with his work on magnetism at low temperatures

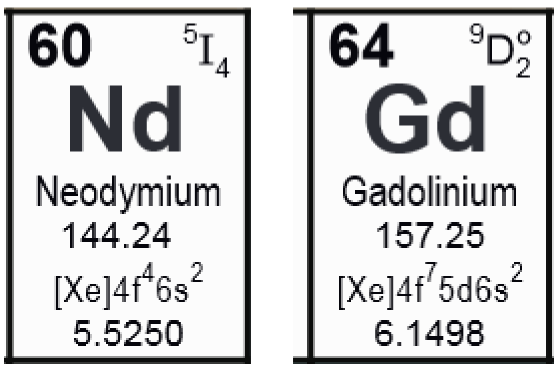
In 1903 he shared the Nobel Prize for work with Marie Curie and Henri Becquerel on radioactivity

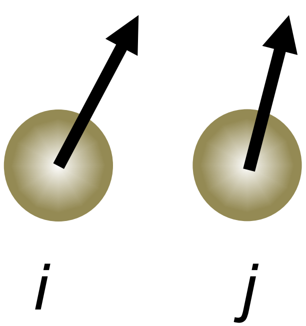

PERIODIC TABLE
Atomic Properties of the Elements
NIST National Institute of Standards and Technology U.S. Department of Commerce
Physical Measurement Laboratory www.nist.gov/pml
Standard Reference Data www.nist.gov/srd
FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS
1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of 133Cs
speed of light in vacuum c 299 792 458 m s−1 (exact)
Planck constant h 6.626 070 15 x 10−34 J Hz−1 (exact)
elementary charge e 1.602 176 634 x 10−19 C (exact)
Avogadro constant NA 6.022 140 76 x 1023 mol−1 (exact)
Boltzmann constant k 1.380 649 x 10−23 J K−1 (exact)
electron volt eV 1.602 176 634 x 10−19 J (exact)
electron mass me 9.109 383 70 x 10−31 kg
energy equivalent mec2 0.510 998 950 MeV
proton mass mp 1.672 621 924 x 10−27 kg
energy equivalent mpc2 938.272 088 MeV
fine-structure constant α 1/137.035 999
Rydberg energy R∞hc 13.605 693 1230 eV
Newtonian constant of gravitation G 6.674 x 10−11 m3 kg−1 s−2
For the most accurate values of these and other constants, visit pml.nist.gov/constants.
Solids
Liquids
Gases
Artificially Prepared
Group
Period
1 H Hydrogen 1.008
2 He Helium 4.0026
3 Li Lithium 6.94
4 Be Beryllium 9.0122
5 B Boron 10.81
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998
10 Ne Neon 20.180
11 Na Sodium 22.990
12 Mg Magnesium 24.305
13 Al Aluminum 26.982
14 Si Silicon 28.085
15 P Phosphorus 30.974
16 S Sulfur 32.06
17 Cl Chlorine 35.45
18 Ar Argon 39.948
19 K Potassium 39.098
20 Ca Calcium 40.078
21 Sc Scandium 44.956
22 Ti Titanium 47.867
23 V Vanadium 50.942
24 Cr Chromium 51.996
25 Mn Manganese 54.938
26 Fe Iron 55.845
27 Co Cobalt 58.933
28 Ni Nickel 58.693
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.630
33 As Arsenic 74.922
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 83.798
37 Rb Rubidium 85.468
38 Sr Strontium 87.62
39 Y Yttrium 88.906
40 Zr Zirconium 91.224
41 Nb Niobium 92.906
42 Mo Molybdenum 95.95
43 Tc Technetium (97)
44 Ru Ruthenium 101.07
45 Rh Rhodium 102.91
46 Pd Palladium 106.42
47 Ag Silver 107.87
48 Cd Cadmium 112.41
49 In Indium 114.82
50 Sn Tin 118.71
51 Sb Antimony 121.76
52 Te Tellurium 127.60
53 I Iodine 126.90
54 Xe Xenon 131.29
55 Cs Cesium 132.91
56 Ba Barium 137.33
72 Hf Hafnium 178.49
73 Ta Tantalum 180.95
74 W Tungsten 183.84
75 Re Rhenium 186.21
76 Os Osmium 190.23
77 Ir Iridium 192.22
78 Pt Platinum 195.08
79 Au Gold 196.97
80 Hg Mercury 200.59
81 Tl Thallium 204.38
82 Pb Lead 207.2
83 Bi Bismuth 208.98
84 Po Polonium (209)
85 At Astatine (210)
86 Rn Radon (222)
87 Fr Francium (223)
88 Ra Radium (226)
104 Rf Rutherfordium (267)
105 Db Dubnium (268)
106 Sg Seaborgium (269)
107 Bh Bohrium (270)
108 Hs Hassium (269)
109 Mt Meitnerium (278)
110 Ds Darmstadtium (281)
111 Rg Roentgenium (282)
112 Cn Copernicium (285)
113 Nh Nihonium (286)
114 Fl Flerovium (289)
115 Mc Moscovium (289)
116 Lv Livermorium (293)
117 Ts Tennessine (294)
118 Og Oganesson (294)
Lanthanides
57 La Lanthanum 138.91
58 Ce Cerium 140.12
59 Pr Praseodymium 140.91
60 Nd Neodymium 144.24
61 Pm Promethium (145)
62 Sm Samarium 150.36
63 Eu Europium 151.96
64 Gd Gadolinium 157.25
65 Tb Terbium 158.93
66 Dy Dysprosium 162.50
67 Ho Holmium 164.93
68 Er Erbium 167.26
69 Tm Thulium 168.93
70 Yb Ytterbium 173.05
71 Lu Lutetium 174.97
Actinides
89 Ac Actinium (227)
90 Th Thorium 232.04
91 Pa Protactinium 231.04
92 U Uranium 238.03
93 Np Neptunium (237)
94 Pu Plutonium (244)
95 Am Americium (243)
96 Cm Curium (247)
97 Bk Berkelium (247)
98 Cf Californium (251)
99 Es Einsteinium (252)
100 Fm Fermium (257)
101 Md Mendelevium (258)
102 No Nobelium (259)
103 Lr Lawrencium (266)
Atomic Number
Ground State
Symbol
Name
Standard Atomic Weight
Ground-state Configuration
Ionization Energy (eV)
†Based upon 12C. () indicates the mass number of the longest-lived isotope.
For the most precise values and uncertainties visit ciaaw.org and pml.nist.gov/data.
NIST SP 966 (July 2019)

Maple 2020

Elemental ferromagnetic materials







Multiple electrons available to make a net total spin *S*

Note that many other atoms have net total spin, but these materials also have an interaction energy for nearest neighbor atoms which can be approximated (in the Heisenberg model) according to

$$\mathcal{H}_{\text{int}} = -J \sum_{ij(neighbors)} \mathbf{S}_i \cdot \mathbf{S}_j$$

Here *J* is an interaction energy determined from quantum mechanics.

First, consider the effects of a magnetic field B on a single atom with spin **S**. The eigenvalue of the quantum operator $\mathbf{S}^2$ is $S(S+1)$. (Here we define spin to be the actual intrinsic spin divided by $h/2\pi$.) Since the atom may have multiple electrons involved, and because some orbital angular momentum may be involved, S may be a half integer or an integer.

The magnetic moment associated with the total spin S is

$\boldsymbol{\mu}=\mu_a\mathbf{S}$ where μ_a is an atom dependent constant. For the pure electron spin case, $\mu_a = \mu_e = -9.2847647043\times10^{-24}\,J\,T^{-1}$.

In the presence of a magnetic field $\mathbf{B}$, the Hamiltonian due to spin is $\mathcal{H}_B = -\mu_a\mathbf{S}\cdot\mathbf{B}$

Continued analysis for non-interacting case – paramagnetic system

$$\mathcal{H}_B = -\mu_a \mathbf{S}\cdot\mathbf{B}$$

Without loss of generality, we can take the magnetic field along the z-axis so that the eigenvalues of the Hamiltonian are

$$\mathcal{H}_B \left| SM \right\rangle = -\mu_a BM \left| SM \right\rangle \quad \text{for} \quad M = -S, -S+1 .... S-1, S$$

Evaluating the canonical partition function for the single atom:

$$Z_1(T) = \sum_{M=-S}^{S} e^{\beta\mu_a BM} = \frac{e^{-\beta\mu_a BS} - e^{\beta\mu_a B(S+1)}}{1-e^{\beta\mu_a B}} \quad \text{where } \beta \equiv \frac{1}{kT}$$

$$Z_1(T) = \frac{\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)}{\sinh\left(\frac{1}{2}\beta\mu_a B\right)} \quad \text{for } N \text{ atoms:} \quad Z(T,N) = \left(\frac{\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)}{\sinh\left(\frac{1}{2}\beta\mu_a B\right)}\right)^N$$

Continued analysis for non-interacting case – paramagnetic system

$$Z(T,N) = \left(\frac{\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)}{\sinh\left(\frac{1}{2}\beta\mu_a B\right)} \right)^N$$

Helmholtz free energy: $F(T,N) = -kT \ln Z(T,N)$

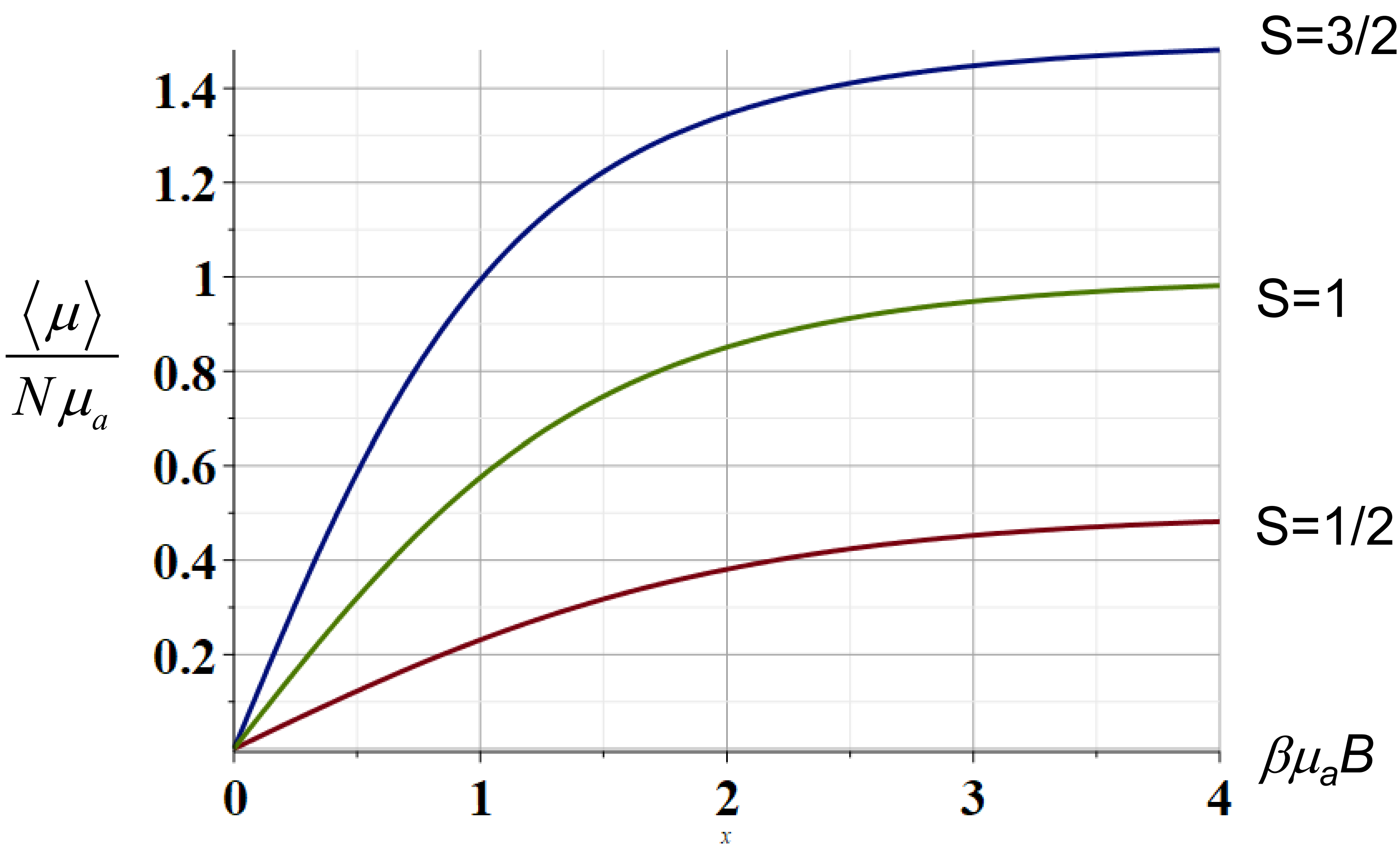
$$F(T,N) = -NkT\left(\ln\left(\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)\right) - \ln\left(\sinh\left(\frac{1}{2}\beta\mu_a B\right)\right)\right)$$

Average magnetic moment of sample along the magnetic field direction:

$$\langle \mu \rangle = -\left(\frac{\partial F}{\partial B}\right)_N = N\mu_a \left(\frac{\left(S+\frac{1}{2}\right)\cosh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)}{\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)} - \frac{\frac{1}{2}\cosh\left(\frac{1}{2}\beta\mu_a B\right)}{\sinh\left(\frac{1}{2}\beta\mu_a B\right)} \right)$$

Average magnetic moment along the magnetic field direction:

$$\langle \mu \rangle = N\mu_a \left(\frac{\left(S+\frac{1}{2}\right)\cosh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)}{\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)} - \frac{\frac{1}{2}\cosh\left(\frac{1}{2}\beta\mu_a B\right)}{\sinh\left(\frac{1}{2}\beta\mu_a B\right)} \right)$$



Average magnetic moment along the magnetic field direction:

$$\langle\mu\rangle = N\mu_a\left(\frac{\left(S+\frac{1}{2}\right)\cosh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)}{\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B\right)} - \frac{\frac{1}{2}\cosh\left(\frac{1}{2}\beta\mu_a B\right)}{\sinh\left(\frac{1}{2}\beta\mu_a B\right)}\right)$$

For small B and/or large T $(\beta\mu_a B << 1)$:

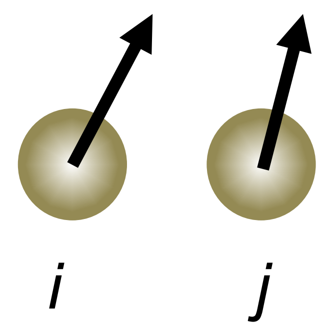
$$\langle\mu\rangle = \left(N\mu_a^2\frac{S(S+1)}{3kT}\right)B = N\chi B$$

Curie susceptibility: $\chi = \mu_a^2\frac{S(S+1)}{3kT}$

Now consider a system in which the spins interact with an external magnetic field and also interact with neighboring spins according to the Heisenberg model

$$\mathcal{H} = -\mu_a \sum_i \mathbf{S}_i \cdot \mathbf{B} - J \sum_{ij(neighbors)} \mathbf{S}_i \cdot \mathbf{S}_j$$

Note that depending upon the material, J>0 when spin alignment is favored (ferromagnetic case) or J<0 when spin anti alignment is energetically favored (antiferromagnetic case).



$$\mathcal{H} = -\mu_a \sum_i \mathbf{S}_i \cdot \mathbf{B} - J \sum_{ij(neighbors)} \mathbf{S}_i \cdot \mathbf{S}_j$$

The exact treatment of this system is difficult. We will make several approximations.

1. Assume that the spin contributions along the B field direction (z) dominates
2. Treat the neighboring spins in an average (mean field) approximation

$$\mathcal{H} = \sum_i \mathcal{H}_i \qquad \mathcal{H}_i \approx -\mu_a S_{iz} B - 2JS_{iz} \sum_{j(neighbors)} S_{jz}$$

Approximation continued --

$$\mathcal{H}_i \approx -\mu_a S_{iz} B - 2JS_{iz} \sum_{j(neighbors)} S_{jz}$$

Suppose that for each site i, the neighbor spins contribute an effective magnetic field parallel to the external field such that $\mu_a B_{neigh} \equiv 2J \sum_{j(neighbors)} S_{jz}$

Then $\mathcal{H}_i \approx -\mu_a S_{iz} \left(B + B_{neigh} \right)$

Calculating the partition function for this approximation

$$\mathcal{H}_i \approx -\mu_a S_{iz}\left(B + B_{neigh}\right) \qquad \text{Denote } B_{tot} = B + B_{neigh}$$

Evaluating the canonical partition function for the single atom:

$$Z_1(T) = \sum_{M=-S}^{S} e^{\beta\mu_a B_{tot} M} = \frac{e^{-\beta\mu_a B_{tot} S} - e^{\beta\mu_a B_{tot}(S+1)}}{1 - e^{\beta\mu_a B_{tot}}} \quad \text{where } \beta \equiv \frac{1}{kT}$$

$$Z_1(T) = \frac{\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B_{tot}\right)}{\sinh\left(\frac{1}{2}\beta\mu_a B_{tot}\right)} \quad \text{for } N \text{ atoms: } \quad Z(T,N) = \left(\frac{\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B_{tot}\right)}{\sinh\left(\frac{1}{2}\beta\mu_a B_{tot}\right)}\right)^N$$

$$F(T,N) = -NkT\left(\ln\left(\sinh\left(\left(S+\frac{1}{2}\right)\beta\mu_a B_{tot}\right)\right) - \ln\left(\sinh\left(\frac{1}{2}\beta\mu_a B_{tot}\right)\right)\right)$$

Average magnetic moment along the magnetic field direction:

$$\langle\mu\rangle = -\left(\frac{\partial F}{\partial B}\right)_N = N\mu_a\left(\left(S+\frac{1}{2}\right)\coth\left(\left(S+\frac{1}{2}\right)\beta\mu_a B_{tot}\right) - \frac{1}{2}\coth\left(\frac{1}{2}\beta\mu_a B_{tot}\right)\right)$$

How can we determine B_{neigh}?

Recall that $\mu_a B_{neigh} \equiv 2J \sum_{j(neighbors)} S_{jz}$

Make the further approximation that

$$\mu_a B_{neigh} \equiv 2J \left\langle \sum_{j(neighbors)} S_{jz} \right\rangle$$

using averaging consistent with canonical distribution.

$$\left\langle S_{jz} \right\rangle = \frac{\langle \mu \rangle}{N\mu_a} = \left(\left(S+\tfrac{1}{2}\right) \coth\left(\left(S+\tfrac{1}{2}\right) \beta\mu_a B_{tot} \right) - \tfrac{1}{2} \coth\left(\tfrac{1}{2} \beta\mu_a B_{tot} \right) \right)$$

$$\Rightarrow B_{neigh} = \frac{2nJ}{\mu_a} \left(\left(S+\tfrac{1}{2}\right) \coth\left(\left(S+\tfrac{1}{2}\right) \beta\mu_a B_{tot} \right) - \tfrac{1}{2} \coth\left(\tfrac{1}{2} \beta\mu_a B_{tot} \right) \right)$$

Here n denotes the number of neighbors.

How can we determine B_{neigh}?

$$\Rightarrow B_{neigh} = \frac{2nJ}{\mu_a}\left(\left(S+\tfrac{1}{2}\right)\coth\left(\left(S+\tfrac{1}{2}\right)\beta\mu_a B_{tot}\right) - \tfrac{1}{2}\coth\left(\tfrac{1}{2}\beta\mu_a B_{tot}\right)\right)$$

where $B_{tot} = B + B_{neigh}$

Obviously, B_{neigh} depends on B and T and must be determined numerically.

Consider the case where the external field is 0.

$$\Rightarrow B_{neigh} = \frac{2nJ}{\mu_a}\left(\left(S+\tfrac{1}{2}\right)\coth\left(\left(S+\tfrac{1}{2}\right)\beta\mu_a B_{neigh}\right) - \tfrac{1}{2}\coth\left(\tfrac{1}{2}\beta\mu_a B_{neigh}\right)\right)$$

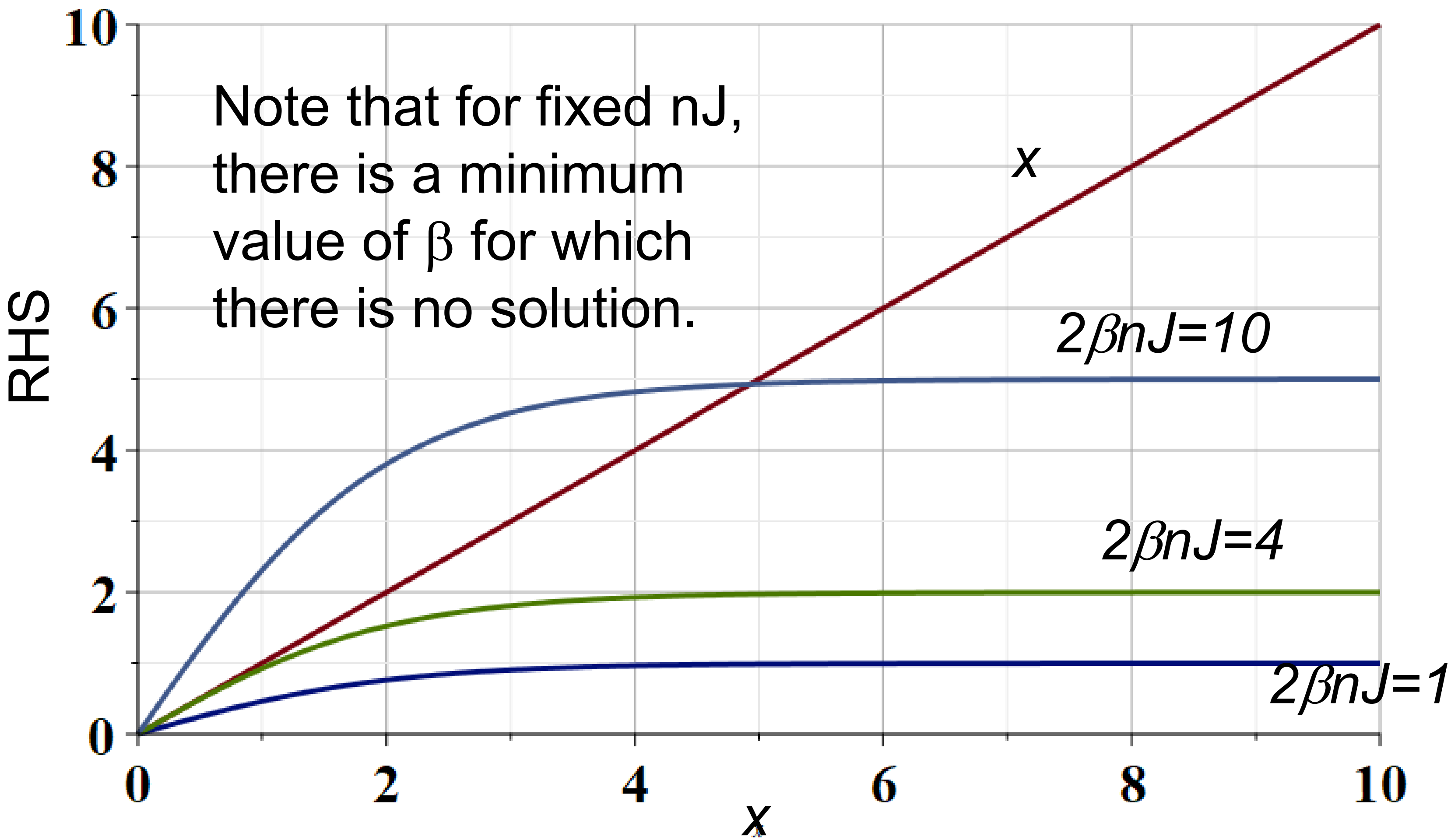
Let $x = \beta\mu_a B_{neigh}$

Equation to solve:

$$x = 2\beta nJ\left(\left(S+\tfrac{1}{2}\right)\coth\left(\left(S+\tfrac{1}{2}\right)x\right) - \tfrac{1}{2}\coth\left(\tfrac{1}{2}x\right)\right)$$

$$x = 2\beta nJ\left(\left(S+\tfrac{1}{2}\right)\coth\left(\left(S+\tfrac{1}{2}\right)x\right)-\tfrac{1}{2}\coth\left(\tfrac{1}{2}x\right)\right)$$

S=1/2



For $2\beta nJ > 2\beta_c nJ$ Solutions exist
For $2\beta nJ < 2\beta_c nJ$ No solutions

This behavior is determined by the linear behavior of the right hand side of the equation

$$RHS(x) = 2\beta nJ\left(\left(S+\tfrac{1}{2}\right)\coth\left(\left(S+\tfrac{1}{2}\right)x\right)-\tfrac{1}{2}\coth\left(\tfrac{1}{2}x\right)\right)$$

$$\approx 2\beta nJ\left(\frac{S(S+1)}{3}x\right)$$

Therefore, in order for $x = 2\beta nJ\left(\frac{S(S+1)}{3}x\right)$,

$$2\beta_c nJ\left(\frac{S(S+1)}{3}\right)=1 \qquad \Rightarrow kT_c = 2nJ\left(\frac{S(S+1)}{3}\right)$$

In the absense of an external magnetic field, at temperatures below the "Curie temperture" $kT_c = 2nJ\left(\frac{S(S+1)}{3}\right)$, the material has a ferromagnetic configuation.

	T_c(K)
Fe	1043
Co	1388
Ni	627
Ga	293