Chapter 8

Canonical Ensemble (E,V,N)

8. Paramagnetism: Quantum-mechanical

We consider a system with N magnetic atoms per unit volume placed in an external magnetic field H. Each atom has an intrinsic magnetic moment $\mu = 2\mu_0 s$ with spin $s = 1/2$.

(a) Energy states. In a quantum-mechanical description, the magnetic moments of the atoms can point either parallel or anti-parallel to the magnetic field.

State	Alignment	Moment	Energy	Probability
$(+)$	Parallel to H	$+\mu$	$-\mu H$	$P_+ = ce^{-\beta\varepsilon_+} = \dfrac{e^{+\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}}$
$(-)$	Anti-parallel to H	$-\mu$	$+\mu H$	$P_- = ce^{-\beta\varepsilon_-} = \dfrac{e^{-\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}}$

We assume here that the atoms interact weakly. One can therefore consider a single atom as a small system and the rest of the atoms as a reservoir in the terms of a canonical ensemble.

(b) Mean magnetic moment. We want to analyze the mean magnetic moment $\langle \mu_H \rangle$ per atom as a function of the temperature T:

$$\langle \mu_H \rangle = \frac{\mu e^{\beta\mu H} - \mu e^{-\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}}, \qquad \langle \mu_H \rangle = \mu \tanh \frac{\mu H}{k_B T}$$

where we used that

$$\tanh y = \frac{e^{y} - e^{-y}}{e^{y} + e^{-y}}, \qquad y = \beta\mu H = \frac{\mu H}{k_B T}$$

(c) Magnetization. We define the magnetization, i.e. the mean magnetic moment per unit volume, as

$$\langle M \rangle = N \langle \mu_H \rangle$$

and analyze its behavior in the limit of high- and of low temperatures.

High-temperature expansion. Large temperatures correspond to $y \ll 1$ and hence to

$$e^{y} = 1 + y + ..., e^{-y} = 1 - y + ...$$

Then,

$$\tanh y = \frac{(1+y+...)-(1-y+...)}{2} \approx y$$

so that

$$\langle \mu_H \rangle = \frac{\mu^2 H}{k_B T}$$

Curie Law. For the magnetic susceptibility χ, defined as $\langle M \rangle = \chi H$, we then have

$$\chi = \frac{N\mu^2}{k_B T}$$

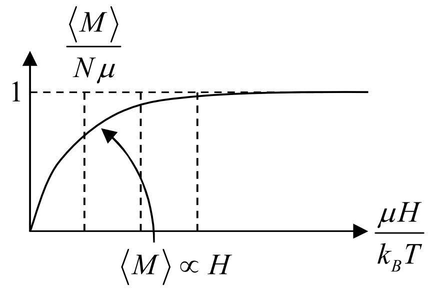
At temperatures high compared to the magnetic energies, $\chi \propto T^{-1}$ which is known as the Curie law.

Low-temperature expansion. Low temperatures correspond to $y \gg 1$,

$$e^{y} \gg e^{-y}, \qquad \tanh y \approx 1$$

and hence $\langle \mu H \rangle = \mu$, $\langle M \rangle = N\mu$

The magnetization saturates at the maximal value at low temperatures independent of H.



As the spins of particles are independent of each other, the partition function of the total system Z_N is equal to the product of the partition functions for spins of individual particle. The partition function for spins of individual particle is

$$Z_i = e^{\mu H/k_BT} + e^{-\mu H/k_BT} = 2\cosh(\mu H/k_BT)$$

Thus, $Z_N = Z_i^N = \left[2\cosh(\mu H/k_BT)\right]^N$

The Helmholtz free energy is

$$F = -k_BT\ln Z_N = -Nk_BT\ln\left[2\cosh(\mu H/k_BT)\right]$$

The entropy is

$$S = \left(-\frac{\partial F}{\partial T}\right)_V = Nk_B\left[\ln\left\{2\cosh(\mu H/k_BT)\right\} - (\mu H/k_BT)\tanh(\mu H/k_BT)\right]$$

Total energy is $U = F + TS = -N\mu H\tanh(\mu H/k_BT)$

Total magnetic moment is

$$M = -\frac{\partial F}{\partial H} = N\mu\tanh(\mu H/k_BT)$$

The specific heat at constant volume c_V is

$$C_V = \left[\frac{\partial U}{\partial T}\right]_V = Nk_B(\mu H/k_BT)^2\sec h^2(\mu H/k_BT)$$

A Two-Level System

Example: A system in thermal equilibrium has energies 0 and E. Calculate partition function of system and hence calculate:

(i) Helmholtz Free energy (*F*)

(ii) Entropy (*S*)

(iii) Internal energy (*U*)

(iv) Specific heat at constant volume c_V discuss the trend of specific heat at

(a) Low temperature and

(b) High temperature

Solution: Let T be the temperature of the system. The partition function Z of the system is

$$Z = e^{0/k_BT} + e^{-E/k_BT} = 1 + e^{-E/k_BT}$$

(i) Free energy F of the system is

$$F = -k_BT \ln Z = -k_BT \ln\left[1 + e^{-E/k_BT}\right]$$

(ii)Entropy S of the system is

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = k_B \ln\left[1 + e^{-E/k_BT}\right] + \frac{E}{T}\frac{1}{e^{E/k_BT} + 1}$$

(iii) Internal energy U is

$$U = F + TS$$

$$= -k_BT \ln\left[1 + e^{-E/kT}\right] + k_BT \ln\left[1 + e^{-E/k_BT}\right] + \frac{E}{e^{E/k_BT} + 1} = \frac{E}{e^{E/k_BT} + 1}$$

(iv) Specific heat at constant volume C_V is

$$c_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = k_B\left(\frac{E}{k_BT}\right)^2 \frac{e^{E/k_BT}}{\left(e^{E/k_BT} + 1\right)^2}$$

(a) At a low temperature $E/k_BT \gg 1$, and equation above reduces to

$$C_V = k_B\left(\frac{E}{k_BT}\right)^2$$

Since with the decrease of T, the function e^{-E/k_BT}, therefore

$C_V \to 0$ when $T \to 0$

(b) At a high temperature $E/k_B T << 1$ and equation reduces to

$C_V = k\left(\frac{E}{k_B T}\right)^2 \frac{1}{4}$ Hence, $C_V \to 0$ when $T \to \infty$

Free Particle in 1D box: Classical Treatment

Example: The Hamiltonian of one-dimensional N free particle is confine in box of length L given by $E(q,p) = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m}\right]$ write down

(a) Expression of partition function

(b) Internal energy of system

(c) Specific heat at constant volume

Solution: (a) $Z_N = \frac{1}{h^N}\int \exp\left(-\left\{\sum_{i=1}^{N}\left[\frac{p_i^2}{2m}\right]\right\}\Big/ k_B T\right) \; dq_i \; dp_i$

$$= \frac{1}{h^N}\prod_{i=1}^{N}\left\{\int_{-\infty}^{\infty} e^{-p_i^2/2mk_B} dp_i \int_0^L dq_i\right\}$$

For evaluation of the first integral of equation let us put $\frac{p_i^2}{2mk_B T} = u$ and $\frac{p_i dp_i}{mk_B T} = du$

Using equations in the first integral equation we have

$$\int_{-\infty}^{\infty} \exp\left(p_i^2 / 2mk_B T\right) dp_i = 2\int_0^{\infty} \exp\left(-p_i^2 / 2mk_B T\right) dp_i$$

$= \sqrt{2mk_B T}\int_0^{\infty} e^{-u} u^{-1/2} = \sqrt{2\pi mk_B T}$ and integration of second integral is L

Partition function of one particle is $Z = \frac{1}{h}\left(2\pi mk_B T\right)^{1/2}(L)$

Partition function of N particle is $Z_N = Z^N = \frac{1}{h^N \lfloor N}\left(2\pi mk_B T\right)^{N/2}(L)^N$

(b) The internal energy $\langle E\rangle = \langle U\rangle = k_B T^2 \frac{1}{Z}\frac{\partial Z}{\partial T}$, $\langle E\rangle = \langle U\rangle = \frac{Nk_B T}{2}$

(c) $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{Nk_B}{2}$

One dimensional Classical Harmonic Oscillator

Example: Total energy of the system of N one dimensional classical oscillator is given by

$$E(q,p)=\sum_{i=1}^{N}\left[\frac{p_i^2}{2m}+\frac{1}{2}m\omega^2 q_i^2\right]$$

where q_i and p_i are position and momentum of the i-th oscillator, respectively.

Write down

(a) Partition function

(b) Helmholtz Free energy

(c) Entropy

(d) Internal energy

(e) Specific heat at constant volume

Solution: (a) The partition function of the system is

$$Z_N=\frac{1}{h^N}\int \exp\left(-\left\{\sum_{i=1}^{N}\left[\frac{p_i^2}{2m}+\frac{1}{2}m\omega^2 q_i^2\right]\right\}\Big/ k_BT\right)\quad dq_i \quad dp_i$$

$$=\frac{1}{h^N}\prod_{i=1}^{N}\left\{\int_{-\infty}^{\infty}e^{-p_i^2/2mk_BT}dp_i\int_{-\infty}^{\infty}e^{-m\omega^2q_i^2/2k_BT}dq_i\right\}$$

For evaluation of the first integral of equation let us put $\frac{p_i^2}{2mk_BT}=u$ and $\frac{p_idp_i}{mk_BT}=du$

Using equations in the first integral equation we have

$$\int_{-\infty}^{\infty}\exp\left(p_i^2/2mk_BT\right)dp_i=2\int_0^{\infty}\exp\left(-p_i^2/2mk_BT\right)dp_i$$

$$=\sqrt{2mk_BT}\int_0^{\infty}e^{-u}u^{-1/2}=\sqrt{2\pi mk_BT}$$

For evaluation of the second integral of equation, let us put

$$\frac{m\omega^2q_i^2}{2k_BT}=u \quad \text{and} \quad \frac{m\omega^2q_idq_i}{k_BT}=du$$

$$\int_{-\infty}^{\infty}\exp\left(-m\omega^2q_i^2/2k_BT\right)dq_i=2\int_0^{\infty}\exp\left(-m\omega^2q_i/mk_BT\right)\quad dq_i$$

$$=\sqrt{\frac{k_BT}{m\omega^2}}\int_{-\infty}^{\infty}e^{-u}u^{-1/2}du=\sqrt{\frac{2\pi k_BT}{m\omega^2}}$$

$$Z_N=\frac{1}{h^N}\left(2\pi mk_BT\right)^{N/2}\left(\frac{2\pi k_BT}{h\omega}\right)^N$$

(b) Free energy F of the system is

$$F = -k_B T \ln Z_N = -Nk_B T \ln\left(\frac{2\pi k_B T}{h\omega}\right)$$

Once the free energy of the system is known, we can calculate other thermodynamical quantities of the system.

(c) Entropy S of the system is

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = Nk_B \ln\left(\frac{2\pi k_B T}{h\omega}\right) + Nk_B$$

(d) Internal energy U is

$$U = F + ST = Nk_B T$$

Thus, the mean energy per oscillator is $k_B T$

(e) Specific heat at constant volume C_V is

$C_V = \frac{\partial U}{\partial T} = Nk_B$ The specific heat at constant volume C_V is independent of the temperature

Quantum Mechanical Harmonic Oscillator: 1D

Example: In quantum mechanics, energy of an oscillator is quantized and the energy of the N such system is given by

$$E_{n_i} = \sum_{i=1}^{N} \hbar\omega\left(n_i + \frac{1}{2}\right)$$

where n_i is an integer; $n_i = 0, 1, 2, 3, ...$ then find

(a) The partition function of the system.

(b) Entropy

(c) Helmholtz free energy

(d) Internal energy

(e) Specific heat at constant volume, also discuss the case for lower temperature and higher temperature.

Solution: (a) $Z_N = \sum_{n_i} \exp\left(-E_{n_i}/k_BT\right) = \sum_{n_i} \exp\left\{-\sum_{i=1}^{N} \hbar\omega\left(n_i + \frac{1}{2}\right)\Big/ k_BT\right\}$

$$= \prod_{i=1}^{N}\left[\sum_{n_i=0}^{\infty} \exp\left\{-\hbar\omega\left(n_i+\frac{1}{2}\right)\Big/ k_BT\right\}\right]$$

We know that $\sum_{n_i=0}^{\infty} \exp\left\{-\hbar\omega\left(n_i+\frac{1}{2}\right)\Big/ k_BT\right\} = \exp\left(-\hbar\omega/2k_BT\right) + \exp\left(-3\hbar\omega/2k_BT\right)........$

$$= \exp\left(-\hbar\omega/2k_BT\right)\left[\frac{1}{1-\exp\left(-\hbar\omega/k_BT\right)}\right] = \frac{\exp\left(-\hbar\omega/2k_BT\right)}{1-\exp\left(-\hbar\omega/k_BT\right)}$$

Thus, the partition function is

$$Z_N = \left[\frac{\exp\left(-\hbar\omega/2k_BT\right)}{1-\exp\left(-\hbar\omega/k_BT\right)}\right]^N \; or = \left(2\sinh\frac{\hbar\omega}{2k_BT}\right)^{-N}$$

(b) Free energy F of the system is

$$F = -k_BT\ln Z_N = -Nk_BT\ln\left[\frac{\exp\left(-\hbar\omega/2k_BT\right)}{1-\exp\left(-\hbar\omega/k_BT\right)}\right]$$

$$= \frac{N\hbar\omega}{2} + Nk_BT\ln\left[1-\exp\left(-\hbar\omega/k_BT\right)\right]$$

Once the free energy of the system is known, we can calculate other thermodynamical quantities of the system.

(c) Entropy S of the system is

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = -Nk_B\ln\left[1-\exp\left(-\hbar\omega/k_BT\right)\right] + \frac{N\hbar\omega/T}{\exp\left(\hbar\omega/k_BT\right)-1}$$

$$= Nk_B\left\{\left(\frac{\hbar\omega}{k_BT}\right)\frac{1}{\exp\left(\hbar\omega/k_BT\right)-1} - \ln\left[1-\exp\left(-\hbar\omega/k_BT\right)\right]\right\}$$

(d) Internal energy U is

$$U = F + ST = N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\exp\left(\hbar\omega/k_BT\right)-1}\right]$$

(e) Specific heat at constant volume C_V is

$$C_V = \frac{\partial U}{\partial T} = N\hbar\omega\frac{\exp\left(\hbar\omega/k_BT\right)}{\left[\exp\left(\hbar\omega/k_BT\right)-1\right]^2}\left(\frac{\hbar\omega}{k_BT^2}\right)$$

$$= Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{\exp(\hbar\omega/k_BT)}{\left[\exp(\hbar\omega/k_BT)-1\right]^2}$$

- At a low temperature, we have $(\hbar\omega/k_BT) >> 1$, and therefore, equation reduces to

$$C_V = Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \exp\left(-\frac{\hbar\omega}{k_BT}\right)$$

Since with the decrease of T, the function $e^{-\hbar\omega/k_BT}$ reduces much faster than the increase of the function $(\hbar\omega/k_BT)^2$, therefore $C_V \to 0$ when $T \to 0$

- At a high temperature, we have $(\hbar\omega/k_BT) << 1$, and therefore, equation reduces to

$$C_V = Nk_B \frac{1+\hbar\omega/k_BT+.....}{(1+\hbar\omega/2k_BT+.....)^2}$$

It gives $C_V \to Nk_B$ when $T \to \infty$ it shows that the classical result for C_V is valid at high temperature.

Example: If Z is partition of one dimensional harmonic oscillator with energy $\left(n+\frac{1}{2}\right)\hbar\omega$ where $n = 0,1,2,3,....$ at equilibrium temperature T.

(a) what is probability that system has energy $\frac{\hbar\omega}{2}$

(b) what is probability that system has energy lower than $4\hbar\omega$

(c) what is probability that system has energy greater than $4\hbar\omega$

Solution: If Z is partition of system what will be probability that system has energy $\frac{\hbar\omega}{2}$ equilibrium temperature T.

Solution: (a) $p(E_i) = \dfrac{\exp-\dfrac{E_i}{k_BT}}{Z}$, $p\left(\dfrac{\hbar\omega}{2}\right) = \dfrac{\exp-\dfrac{\hbar\omega}{2k_BT}}{Z}$

(b) System has smaller thus energy $4\hbar\omega$ possible energy is $\frac{\hbar\omega}{2}, \frac{3\hbar\omega}{2}, \frac{5\hbar\omega}{2}, \frac{7\hbar\omega}{2},$

so, $$p(E < 4\hbar\omega) = \frac{\exp-\frac{\hbar\omega}{2k_BT}+\exp-\frac{3\hbar\omega}{2k_BT}+\exp-\frac{5\hbar\omega}{2k_BT}+\exp-\frac{7\hbar\omega}{2k_BT}}{Z}$$

$$p(E > 4\hbar\omega) = 1 - p(E < 4\hbar\omega)$$

$$p\left(E>4\hbar\omega\right)=1-\left[\frac{\exp-\frac{\hbar\omega}{2k_BT}+\exp-\frac{3\hbar\omega}{2k_BT}+\exp-\frac{5\hbar\omega}{2k_BT}+\exp-\frac{7\hbar\omega}{2k_BT}}{Z}\right]$$

Classical Paramagnetic substance: Continuous System

Example: A paramagnetic system consists of N magnetic dipoles. Each dipole carries magnetic moment μ which can be treated classically. If the system at finite temperature T in a uniform magnetic field H.

(a) Find partition function

(b) Internal energy

(c) Find average magnetic moment.

(d) Write down expression of average magnetization.

Solution: (a) For paramagnetic substance interaction energy is given by $E_i=-\mu\cdot H$ which equivalent to $E=-\mu H\cos\theta$ (we are in three dimensional system so θ and φ both are classical state of system in spherical coordinate system)

Partition function for one dipole moment is given by $Z_1=\int\limits_{\phi=0}^{2\pi}\int\limits_{\theta=0}^{\pi}e^{\mu H\beta\cos\theta}\sin\theta d\theta d\phi$ where

$$\beta=\frac{1}{k_BT}$$

And for N number of dipole partition function is $Z_N=\left(2\pi\times\int\limits_0^{\pi}e^{\mu\beta H\cos\theta}\sin\theta d\theta\right)^N$

$$=\left[\frac{2\pi}{\mu\beta H}\left[e^{\beta\mu H}-e^{-\beta\mu H}\right]\right]^N\Rightarrow Z_N=\left[\frac{4\pi}{\mu\beta H}\sinh\left(\beta\mu H\right)\right]^N$$ at equilibrium temperature T where

(b) $F=-Nk_BT\ln\left[\frac{4\pi}{\mu\beta H}\sinh\left(\beta\mu H\right)\right]$

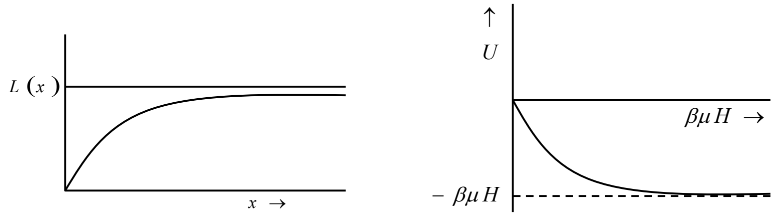
$$U=k_BT^2\frac{\partial\ln Z}{\partial T}=-\left(\frac{\partial\ln Z}{\partial\beta}\right)\Rightarrow U=-N\mu H\left[\cot h\beta\mu H-\frac{1}{\beta\mu H}\right]$$

One can write the expression in term of Langevin function which is given by

$\left(L\left(x\right)=\coth x-\frac{1}{x}\right)$ where $x=\beta\mu H\Rightarrow\left\langle U\right\rangle=-N\mu HL\left(x\right)$

The plot of

Langevin function and internal energy is given below



(c) average magnetic moment for a paramagnetic substance

$$P(-\mu\cdot H)=\frac{e^{-\beta(-\mu H)\cos\theta}}{Z}=\frac{e^{\beta\mu H\cos\theta}}{Z}$$

Assume magnetic field is in z direction so all component of μ is effectively in z direction

$$\mu_{effective}=\{\mu=\mu_Z=\mu\cos\theta\}$$

$$\langle\mu\rangle=\frac{\int_0^{2\pi}\int_0^{\pi}\mu\cos\theta e^{\beta\mu H\cos\theta}\sin\theta d\theta d\phi}{\int_0^{\pi}\int_0^{\pi}e^{-\mu H\beta\cos\theta}\sin\theta d\theta d\phi}$$ put $\beta\mu\cos\theta=t$ so $-\beta\mu\sin\theta d\theta=dt$

$$\langle\mu\rangle=\mu\left[\coth(\beta\mu H)-\frac{1}{\beta\mu H}\right]$$

(d) The average magnetization is given by

$$M=N\langle\mu\rangle=N\mu\left[\coth(\beta\mu H)-\frac{1}{\beta\mu H}\right]$$

Gravitational Field

Example: Consider a system of N particles, each of mass m, enclosed in an infinitely long cylindrical container placed in a uniform gravitational field. The system is in thermal equilibrium. Obtain expressions for the

(a) classical partition function,

(b) Helmholtz free energy

(c) Entropy

(d) Internal energy and

(e) Specific heat of the system

Solution: (a)Let us take consider a cylinder whose axis is along the z-axis of the Cartesian coordinate system and base is in the plane z = 0. Suppose there are N identical particles in a system. Each of the particles is moving independently and there is no potential energy. Total energy of a particle is

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz$$

Thus, the partition function of a single particle is

$$Z_1 = \frac{1}{h^3}\int\int\int\int\int\int e^{-E/k_BT} dxdydz \quad dp_x dp_y dp_z$$

$$= \frac{1}{h^3}\int\int\int\int\int\int e^{-\left(p_x^2+p_y^2+p_z^2\right)/2mk_BT} e^{-mgz/k_BT} dxdydzdp_x dp_y dp_z$$

$$\frac{\sigma}{h^3}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\int_0^\infty e^{-mgz/k_BT}dz = \frac{\sigma k_bT}{mg}\left(2\pi mk_BT\right)^{3/2}$$

where σ is cross section of the container. As the particles are independent of each other, the partition function of the total system Z_N is equal to the product of the partition functions for individual particle. Thus, we have

$$Z_N = \frac{1}{N!}\left(Z_1\right)^N = \frac{1}{N!}\left(\frac{\sigma k_BT}{mg}\right)^N\left(\frac{2\pi mk_BT}{h^2}\right)^{3N/2}$$

(b) The Helmholtz free energy F of the system is

$$F = -k_BT\ln\left(Z_N\right) = -Nk_BT\ln\left[\frac{\sigma k_BT}{Nmg}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right]$$

(c)The entropy S of the system is

$$S = -\frac{\partial F}{\partial T} = Nk_B\ln\left[\frac{\sigma k_BT}{Nmg}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right] + \frac{5}{2}NkT$$

(d)The internal energy U is $U = F + ST = \frac{5}{2}Nk_BT$

(e) The specific heat C_V is $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{5}{2}Nk_B$

Linear Potential

Example: A particle is confined to the region x ≥ 0 by a potential which increases linearly as *u*(*x*) = $u_0 x$. find the mean position of the particle at temperature *T*.

Solution: Partition function is given by $Z = \frac{1}{h}\int e^{-\frac{p^2}{2mk_BT}}dp\int e^{-\frac{u_0 x}{k_BT}}dx$

$$\langle x\rangle = \int xp(x)dxdp_x = \frac{\int\int xe^{-\frac{p^2}{2mk_BT}}dp\, e^{-\frac{u_0x}{k_BT}}dx}{\int\int e^{-\frac{p^2}{2mk_bT}}dp\; e^{-\frac{u_0x}{k_BT}}dx} = \frac{\int_0^\infty xe^{-\frac{u_0x}{k_BT}}dx}{\int_0^\infty e^{-\frac{u_0x}{k_BT}}dx} = \frac{\left(\frac{k_BT}{\mu_0}\right)^2\int_0^\infty te^{-t}dt}{\left(\frac{k_BT}{\mu_0}\right)\int_0^\infty e^{-t}dt} = \frac{k_BT}{u}$$

Example: A system consists of N noninteracting, distinguishable two-level atoms. Each atom can exist in one of two states, $E_0 = 0$, and $E_1 = \varepsilon$. The number of atoms in energy level E_1 is n_1. The internal energy of the system is $U = n_0E_0 + n_1E_1$.

(a) Compute the entropy of the system as a function of internal energy.

(b) Compute the heat capacity of a fixed number of atoms, N.

Solution: Since $E_0 = 0$ the energy U can be realized in $U/\varepsilon \equiv n_1$ particles are in the state 1, and $(N - U/\varepsilon) = N - n_1$ particles are in the state 0. The number of ways to do that is

$$W = \frac{N!}{n_1!(N-n_1)!}$$

Consequently, $$\frac{S}{k} \approx \ln\frac{N!}{(N-n_1)!} \approx N\ln N - N - n_1\ln n_1 + n_1 - (N-n_1) + (N-n_1)$$

Finally, $\frac{S}{k} \approx N\ln N - \frac{U}{\varepsilon}\ln\frac{U}{\varepsilon} - \left(N - \frac{U}{\varepsilon}\right)\ln\left(N - \frac{U}{\varepsilon}\right)$

To find temperature we do usual procedure

$$\frac{1}{T} = \frac{\partial S}{\partial U} \approx \frac{k}{\varepsilon}\ln\frac{N\varepsilon - U}{U}$$

As result, $U = \frac{N\varepsilon}{e^{\varepsilon/kT}+1}$, $C = Nk\left(\frac{\varepsilon}{kT}\right)^2\frac{e^{\varepsilon/kT}}{\left(e^{\varepsilon/kT}+1\right)^2}$

Example: Consider a lattice with N spin-1 atoms with magnetic moment μ. Each atom can be in one of 3 spin states, $S_z = -1, 0, +1$. Let n_{-1}, n_0 and n_1 denote the respective number ofatoms in each of those spin states. Find the total entropy and the configuration which maximizesthe total entropy. What is the maximum entropy? (Assume that no magnetic field is present, so all atoms have the same energy. Also assume that atoms on different lattice sites cannot beexchanged, so they are distinguishable).

Solution: We have, $W = \dfrac{N!}{n_{-1}!n_1!(N - n_{-1} - n_1)}$

$$\ln W \approx N \ln N - n_{-1} \ln n_{-1} - (N - n_{-1} - n_{-1}) \ln (N - n_{-1} - n_1)$$

Differentiating this function by $n_{-1}$and $n_1$and equating the derivatives to 0 we get:

$$n_1 = (N - n_1 - n_{-1}) = n_{-1} \to n_1 = n_0 = n_{-1} = N/3$$

The maximum entropy is

$S_{\max} = kN \ln 3$

Example: Consider a one-dimensional lattice with N lattice sites and assume that i-th lattice site has spin $s_i \pm 1$. The Hamiltonian describing this lattice is

$$H = -\varepsilon \sum_{i=1}^{N} s_i s_j + 1$$

Assume periodic boundary condition, so $sN + 1 = s_1$. Compute the correlation function $\langle s_1 s_2 \rangle$. How does it behave at very high temperature and at very low temperature?

Solution: We have

$$Z_N(T) = \sum_{s_1=\pm1} \ldots \sum_{s_1=\pm1} \exp\left(\beta\varepsilon \sum_i s_i s_j + 1\right)$$

As it is recommended in the book [1], we introduce the matrix

$$\overline{P} = \begin{pmatrix} e^{\beta\varepsilon} & e^{-\beta\varepsilon} \\ e^{-\beta\varepsilon} & e^{\beta\varepsilon} \end{pmatrix} = e^{\beta\varepsilon} I + e^{-\beta\varepsilon}\sigma_1$$

We have, $\langle s_i | \overline{P} | s_{j+1} \rangle = e^{\beta s_i s j+1}$

Then, $Z_N(T) \sum_{s_1=\pm1} \ldots \sum_{sN=\pm1} \langle s_1 | \overline{P} | s_2 \rangle \langle s_2 | \overline{P} | s_3 \rangle \ldots \langle sN | \overline{P} | s_1 \rangle = Tr\overline{P}^N$

The matrix $\overline{P}$ has eigenvalues

$\lambda_1 = \cosh \beta\varepsilon, \quad \lambda_2 = 2\sinh \beta\varepsilon$

Thus, $Z_N(\beta) = 2^N \left(\cosh^N \beta\varepsilon + \sinh^N \beta\varepsilon\right)$

We have $\langle s_i s_j + 1\rangle = \dfrac{1}{N\varepsilon}\dfrac{\partial \ln Z_N}{\partial \beta} = \dfrac{\cosh^{N-1}(\beta\varepsilon)\sinh^{N-1}(\beta\varepsilon)\cosh(\beta\varepsilon)}{\cosh^N(\beta\varepsilon)+\sinh^N(\beta\varepsilon)}$

At low temperature, $\beta\varepsilon \gg 1, \cosh(\beta\varepsilon) \approx \sinh(\beta\varepsilon)$ and $\langle s_i s_{j+1}\rangle = 1$. Thus, we have ferromagnet ordering.

At high temperature, $\cosh(\beta\varepsilon) \to 1, \sinh(\beta\varepsilon) \to 0 \to \langle s_i s_{j+1}\rangle \beta \ll 1$

Example: In the mean field approximation to the Ising lattice, the order parameter, $\langle s\rangle$ satisfied the equation

$$\langle s\rangle = \tanh\left(\langle s\rangle \frac{T_C}{T}\right)$$

where $T_c = \nu\varepsilon/2k$ where ε is the strength of the coupling between lattice sites and is the number of nearest neighbors.

(a) Show that $\langle s\rangle$ is the following temperature dependence

$$\langle s\rangle \approx \begin{cases} 1 - e^{-2T_c/T}, & T \to 0 \\ \sqrt{3(1 - T/T_C)}, & T \to T_C \end{cases}$$

(b) Compute the jump in the heat capacity at $T = T_C$

(c) Compute the magnetic susceptibility, $\chi(T, N)_{B=0}$, in the neighborhood of T_C both for $T > T_c$ and $T < T_c$. What is the critical exponent for both cases?

Solution: Since $\tan\xi = 1 - 2e^{-2\xi}$ at large ξ, we get

$$(s) \approx 1 - 2e^{2\langle s\rangle T_c/T} \to (s) \approx 1 - 2e^{-2T_c/T}$$

At small ξ, $\tanh\xi \approx \xi - \xi^3/3$, we obtain

$$\langle s\rangle \approx \langle s\rangle \frac{T_C}{T}\frac{\langle s\rangle^3}{3}\left(\frac{T_C}{T}\right)^3. \text{ Thus, } \langle s\rangle \approx \sqrt{3(1 - T/T_C)}$$

(b) The Hamiltonian is

$$H = -\sum_{i=1}^{N} E(\varepsilon, B) s_i, \qquad E(\varepsilon, B) = \frac{v\varepsilon}{2}\langle s\rangle + \mu B$$

Thus $U = -NE\langle s\rangle = -NE\langle s\rangle$, and

$$C = -N\left(\frac{\partial E(\varepsilon, B)\langle s\rangle}{\partial T}\right)_{N,B} = -N\left[E + \langle s\rangle \frac{\partial E}{\partial\langle s\rangle}\right]\left(\frac{\partial\langle s\rangle}{\partial T}\right)_{N,B}$$

At $T \to T_C - 0$ and $B = 0$ we get

$$\langle s\rangle = \sqrt{3(1 - T/T_C)} \quad \to C_{T_C} - 0 = \frac{3}{2}\frac{Nv\varepsilon}{T_C}$$

At $T > T_C$ the average spin is zero, thus the jump in specific heat is given by $C_{T_C} - 0$

(c) To get magnetic susceptibility we have to differentiate the magnetic moment $N = N\mu\langle s\rangle$ with respect to B:

$$\chi = N\mu\left(\frac{\partial\langle s\rangle}{\partial B}\right)_{N,B\to 0}$$

Defining $\eta = \left(\partial\langle s\rangle / \partial B\right)_{N,B\to 0}$ we get the following equation at $B \to 0$

$$\eta = \frac{1}{\cosh^2\left(\langle s\rangle T_C / T\right)}\left[\frac{\beta v\varepsilon}{2}\eta + \beta\mu\right]$$

Its solution is $\eta = \dfrac{2\beta\mu}{\cosh^2\left(\langle s\rangle T_C / T\right) - T_C / T}$. Finally, $\chi = \dfrac{N\mu^2}{v\varepsilon}\dfrac{T_C / T}{\cosh^2\left(\langle s\rangle T_C / T\right) - T_C / T}$

About T_C we have $\langle s\rangle = 0$, and $\chi = \dfrac{N\mu^2}{v\varepsilon}\dfrac{T_C}{T - T_C}$

Below T_C we get

$$\cosh^2\left(\langle s\rangle T_C / T\right) \approx \left[1 + \frac{\langle s\rangle^2}{2}\left(\frac{T_C}{T}\right)^2\right]^2 \approx 1 + 3\left(1 + \frac{T}{T_C}\right)$$

As a result, below T_C, $\chi = \dfrac{N\mu^2}{v\varepsilon}\dfrac{T_C}{2(T_C - T)}$

Thus, there is a divergence at $T \to T_C, \chi \propto |T - T_C|^{-1}$ with critical exponent equal to -1

Example: The Hamiltonian of two particles, each of mass m, is

$H(q_1, p_1; q_2, p_2) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + k\left(q_1^2 + q_2^2 + \frac{1}{4}q_1 q_2\right)$, where $k > 0$ is a constant. The value of the partition function

$$Z(\beta) = \int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dp_1 \int_{-\infty}^{\infty} dq_2 \int_{-\infty}^{\infty} dp_2 e^{-\beta H(q_1, p_1; q_2, p_2)}$$

Solution: $z(\beta) = \int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 e^{-\beta H(q_1, p_1, q_2, p_2)}$

$$z(\beta) = \int_{-\infty}^{\infty} e^{-\beta \frac{p_1^2}{2m}} dp_1 \int_{-\infty}^{\infty} e^{-\beta \frac{p_2^2}{2m}} dp_2 \int_{-\infty}^{\infty}\int_{\infty}^{\infty} e^{-\beta k\left(q_1^2 + q_2^2 + \frac{q_1 q_2}{4}\right)} dq_1 dq_2$$

$$= \sqrt{\frac{\pi}{\beta / 2m}} \sqrt{\frac{\pi}{\beta / m}} = \frac{2\pi m}{\beta} \cdot 2 \cdot \frac{\pi}{\beta k} \sqrt{\frac{16}{63}} = \frac{2m\pi^2}{k\beta^2} \sqrt{\frac{64}{63}}$$

Using Jacobian Transformation, $q_1 = u + v$

$$q_1^2 + q_2^2 + \frac{q_1 q_2}{4} = u^2 + v^2 + 2uv + u^2 + v^2 - 2uv + \frac{u^2 - v^2}{4}$$

$$= 2\left[u^2 + v^2\right] + \frac{u^2 - v^2}{4} = \frac{8u^2 + 8v^2 + u^2 - v^2}{4} = \frac{9u^2 + 7v^2}{4}$$

$$q_2 = u - v \qquad u = \frac{q_1 + q_2}{2} \qquad v = \frac{q_1 - q_2}{2}$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta k\left(q_1^2 + q_2^2 + \frac{q_1 q_2}{4}\right)} dq_1 dq_2 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} J(4,0) e^{\frac{-\beta k}{4}\left(9u^2 + 7v^2\right)} du dv$$

$$J(u,v) = \begin{vmatrix} 1 & 1 \\ 1 & -1 \end{vmatrix} = 2 = 2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-7\beta \frac{k}{4} u^2} du dv$$

$$= 2 \cdot \sqrt{\frac{\pi u}{9\beta k}} \sqrt{\frac{\pi u}{7\beta k}} = 2 \cdot \frac{\pi}{\beta k} \cdot \sqrt{\frac{16}{63}} = \frac{\pi}{\beta k} \sqrt{\frac{64}{63}}$$