BHARATHIDASAN UNIVERSITY

Tiruchirappalli- 620024
Tamil Nadu, India

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Dr. M. Senthilvelan
Professor
Department of Nonlinear Dynamics

UNIT - IV

APPLICATIONS

The heat capacity of solids

- **Einstein model**
- **Debye model**

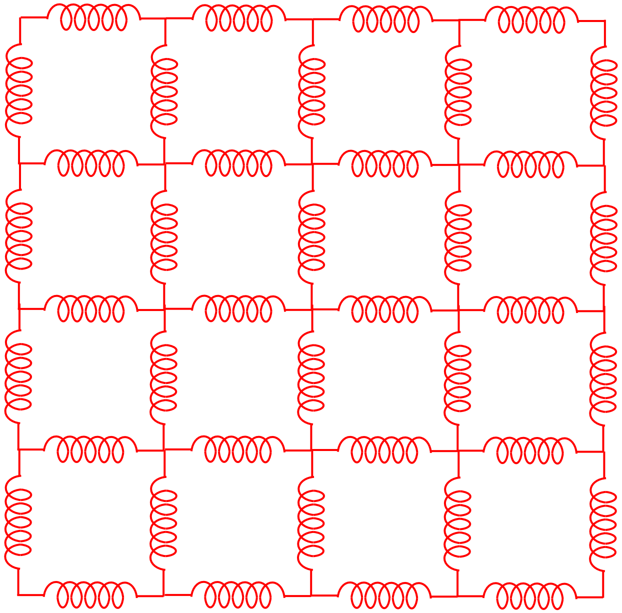
The heat capacity of solids

We have discussed how to calculate the heat capacity of an ideal gas. Now we shall try to understand the heat capacity of a solid using statistical mechanics.

Let us summarize the experimental facts.

(i) Around room temperature ordinary simple solids have a molar heat (heat capacity / mole) of about 3NK = 25 J/ mol. This that is called Dulong - Petit law.

(ii) At low temperatures, the molar heat decreases in proportional to T^3.



Einstein Model

- Just as the motion of atoms contributes to the heat capacity of a gas, we expect that the motion of atoms (or) ions will contribute to the heat capacity of a solid.
- The ideal solid is a crystal, where atoms are arranged periodically in a lattice.
- In a simple cubic lattice, eight neighbouring atoms sit at the corners of a cube.
- The atoms can move around their equilibrium positions which are called of lattice points.
- Owing to the surrounding atoms, the potential energy of an atom is lowest at its lattice point.
- We can depict the situation schematically as one which atoms are connected by springs as shown in the figure.

In this model, the motion of each atom is a harmonic oscillation. Let the angular frequency of the oscillation be ω in all three directions, $x, y\ and\ z$. Each atom then has an energy

$$E_{n_x,n_y,n_z} = (\underbrace{n_x+n_y+n_z}_{\text{Quantum numbers}} + \overbrace{\frac{3}{2}}^{\text{Ground state energy}})\hbar\omega$$

Partition Function:

The energy levels of a crystal containing N atoms are the same as those for a set of 3N independent simple harmonic oscillators having a frequency γ. The possible energy levels associated with this frequency are given by the quantum theory of simple harmonic oscillator as

$$E_n = \left(n \quad + \frac{1}{2}\right) h\gamma \ , \qquad n \quad = 0,1,2, \ldots \qquad (1)$$

The energy of the crystal

$$E_{n_j} = \sum_{j=1}^{3N} \left(n_j + \frac{1}{2}\right) h\gamma_j \ , \qquad (2)$$

The partition function is a sum over all micro states and is given by

$$z = \sum_{\substack{micro \\ states}} e^{-\beta E_{n_j}} \qquad (3)$$

- Summing over are all microstates means that the sum is to be performed over all possible sets of integers. That is, for each normal mode of frequency ν_j , the sum is carried out over all integers from zero to infinity.
- Substituting (2) into (3), we find

$$z = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \dots \sum_{n_{3N}=0}^{\infty} e^{-\beta \sum_{j=1}^{3N} \left(n_j + \frac{1}{2}\right) h\nu_j} \qquad (4)$$

- Now let us define E_0 by

$$E_0 = \frac{1}{2} \sum_{j=1}^{3N} h\nu_j \qquad (zero\ point\ energy) \qquad (5)$$

Rewriting (4)

$$z = e^{-\beta E_0} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \dots \sum_{n_{3N}=0}^{\infty} e^{-\beta \sum_{j=1}^{3N} n_j h\nu_j} \qquad (6)$$

- Equation (6) looks complicated but it can be easily simplified.
- Since we can write the exponential of a sum is the product of the exponentials of the factors.
- Hence we can reduce the multiple sum to a product of sums all of which are a like except for the subscript ‘j’ on the frequencies.
- So equation (6) be comes

$$z = e^{-\beta E_0} \sum_{n_1=0}^{\infty} e^{-\beta n_1 h\nu_1} \sum_{n_2=0}^{\infty} e^{-\beta n_2 h\nu_2} \ldots\ldots \sum_{n_{3N}=0}^{\infty} e^{-\beta n_{3N} h\nu_{3N}} \qquad (7)$$

- Since all the sums have the same form, the subscript on the n_s can be thrown away and (7) can be written as a product of similar sums with one factor for each frequency.

$$z = e^{-\beta E_0} \prod_{j=1}^{3N} \sum_{n=0}^{\infty} e^{-\beta n h\nu_j} \qquad (8)$$

- The infinite sum over n can be easily performed.
- If x_j is defined by

$$x_j = e^{-\beta h\nu_j} \tag{9}$$

Then

$$\sum_{n=0}^{\infty} e^{-\beta n h\nu_j} = \sum_{n=0}^{\infty} x_j^n \tag{10}$$

$$\sum_{n=0}^{\infty} x_j^n = 1 + x_j + x_j^2 + x_j^3 + \ldots. = \frac{1}{1 - x_j}$$

$$\sum_{n=0}^{\infty} e^{-\beta n h\nu_j} = \frac{1}{1 - e^{-\beta h\nu_j}} \tag{11}$$

Substituting this into (8) , we obtain the partition function as

$$z = e^{-\beta E_0} \prod_{j=1}^{3N} \sum_{n=0}^{\infty} e^{-\beta n h\nu_j} = e^{-\beta E_0} \prod_{j=1}^{3N} \frac{1}{1 - e^{-\beta h\nu_j}}$$

- Recall the connection between Helmholtz free energy and the partition function

$$F = -KT \log z$$

$$\log z = \log\left[e^{-\beta E_0}\prod_{j=1}^{3N}\frac{1}{1-e^{-\beta h\nu_j}}\right]$$

$$\log z = \log\left[e^{-\beta E_0}\right] + \log\left[\prod_{j=1}^{3N}\frac{1}{1-e^{-\beta h\nu_j}}\right]$$

$$\log z = -\beta E_0 + \log\left\{\frac{1}{1-e^{-\beta h\nu_1}}\times\frac{1}{1-e^{-\beta h\nu_2}}\times \quad \dots \quad \times\frac{1}{1-e^{-\beta h\nu_{3N}}}\right\}$$

$$\log z = -\beta E_0 + \log\left[\frac{1}{1-e^{-\beta h\nu_1}}\right] + \log\left[\frac{1}{1-e^{-\beta h\nu_2}}\right] + \cdots + \log\left[\frac{1}{1-e^{-\beta h\nu_{3N}}}\right]$$

$$\log z = -\beta E_0 - \log\left(1-e^{-\beta h\nu_1}\right) - \log\left(1-e^{-\beta h\nu_2}\right) + \cdots - \log\left(1-e^{-\beta h\nu_{3N}}\right)$$

$$\log z = -\beta E_0 - \sum_{j=1}^{3N}\log\left(1-e^{-\beta h\nu_j}\right)$$

$$F = E_0 + KT\sum^{3N}\log\left(1-e^{-\beta h\nu_j}\right)$$

Einstein Model

- Einstein treated the nature of the atoms in the solid as if they will oscillate as N independent oscillators. We expect a contribution to the free energy in the form

$$F = NE_0 + KT \sum_j \log\left(1 - e^{-\beta h \nu_j}\right),$$

where the sum is over the 3N vibrational modes.

- The term NE_0 is energy of interaction between atoms in their equilibrium positions and indeed the zero point energy of the oscillators.
- In Einstein model all the frequencies are taken to be the same and given the value ν, the Einstein frequency. The free energy becomes

$$F = NE_0 + KT\left[\log\left(1 - e^{-\beta h\nu}\right) + \log\left(1 - e^{-\beta h\nu}\right) + \cdots + \log\left(1 - e^{-\beta h\nu}\right)\right]$$

$$F = NE_0 + KT\left[3N \log\left(1 - e^{-\beta h\nu}\right)\right]$$

$$F = NE_0 + 3NKT \log\left(1 - e^{-\beta h\nu}\right)$$

Derivation of C_V:

Home work

The heat capacity is obtained by differentiating twice the free energy respect to T.

$$C_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_v$$

$$F = NE_0 + 3NKT\log\left(1 - e^{-\beta h\nu}\right) = NE_0 + 3NKT\log\left(1 - e^{-\beta\hbar\omega}\right)$$

$$\frac{\partial F}{\partial T} = 3NK\left\{\log\left(1-e^{-\beta\hbar\omega}\right) + \frac{T(-)e^{-\beta\hbar\omega}\left(\frac{\hbar\omega}{KT^2}\right)}{(1-e^{-\beta\hbar\omega})}\right\}$$

$$\frac{\partial F}{\partial T} = 3NK\left\{\log\left(1-e^{-\beta\hbar\omega}\right) - \frac{\hbar\omega}{KT}\frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})}\right\}$$

$$\frac{\partial^2 F}{\partial T^2} = 3NK\left\{\frac{-e^{-\beta\hbar\omega}\frac{\hbar\omega}{KT^2}}{1-e^{-\beta\hbar\omega}} + \frac{\hbar\omega}{KT^2}\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} - \frac{\hbar\omega}{KT}\frac{e^{-\beta\hbar\omega}\left(\frac{\hbar\omega}{KT^2}\right)}{1-e^{-\beta\hbar\omega}}\right.$$

$$\left. + \frac{\hbar\omega}{KT}\frac{e^{-\beta\hbar\omega}(-)e^{-\beta\hbar\omega}\left(\frac{\hbar\omega}{KT^2}\right)}{(1-e^{-\beta\hbar\omega})^2}\right\}$$

$$\frac{\partial^2 F}{\partial T^2} = 3NK\left\{\frac{-\hbar^2\omega^2}{K^2T^3}\,\frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})} - \frac{\hbar^2\omega^2}{K^2T^3}\frac{e^{-2\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}\right\}$$

$$\frac{\partial^2 F}{\partial T^2} = \frac{-3NK\hbar^2\omega^2 e^{-\beta\hbar\omega}}{K^2T^3(1-e^{-\beta\hbar\omega})}\left\{1+\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right\}$$

$$\frac{\partial^2 F}{\partial T^2} = \frac{-3NK\hbar^2\omega^2 e^{-\beta\hbar\omega}}{K^2T^3(1-e^{-\beta\hbar\omega})} \times \frac{1}{1-e^{-\beta\hbar\omega}}$$

The heat capacity is obtained by differentiating twice the free energy respect to T.

$$C_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_v = 3NK\left(\frac{\hbar\omega}{KT}\right)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

Limiting Cases:

(i) At high temperatures $KT > \hbar\omega$ $\quad C_v = 3NK.$

(ii) At low temperatures $KT < \hbar\omega$ $\quad C_v = e^{-\beta\hbar\omega}.$

High Temperature Limit :

$$C_v = 3NK\left(\frac{\hbar\omega}{KT}\right)^2 \frac{e^{\frac{\hbar\omega}{KT}}}{\left(e^{\frac{\hbar\omega}{KT}} - 1\right)^2}$$

Case $KT > \hbar\omega$

$$C_v = 3NK\left(\frac{\hbar\omega}{KT}\right)^2 \times \frac{1 + \frac{\hbar\omega}{KT} + \frac{1}{2}\left(\frac{\hbar\omega}{KT}\right)^2 + \cdots}{\left[1 + \frac{\hbar\omega}{KT} + \frac{1}{2}\left(\frac{\hbar\omega}{KT}\right)^2 + \cdots - 1\right]^2}$$

$$C_v = 3NK\left(\frac{\hbar\omega}{KT}\right)^2 \times \frac{1 + \frac{\hbar\omega}{KT}}{\left(\frac{\hbar\omega}{KT}\right)^2}$$

✓

$$C_v = 3NK\left(1 + \frac{\hbar\omega}{KT}\right) = 3NK.$$

Low Temperature Limit :

Case $KT < \hbar\omega$

$$C_v = 3NK\left(\frac{\hbar\omega}{KT}\right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

$$C_v = 3NK\left(\frac{\hbar\omega}{KT}\right)^2 \times \frac{e^{\frac{\hbar\omega}{Kt}}}{e^{\frac{2\hbar\omega}{KT}}}$$

$$C_v = 3NK\left(\frac{\hbar\omega}{KT}\right)^2 e^{-\frac{\hbar\omega}{KT}} \propto e^{-\beta\hbar\omega}$$

✗

Failure :

- Experimental results show that at low temperatures $C_v \propto T^3$.

Paramagnetism

- Consider a system consisting of N non interacting atoms in a substance at absolute temperature T and placed in an external magnetic field $\hat{\mathrm{H}}$ pointing along the z-direction.
- Then the magnetic energy of an atom can be written as

$$\epsilon = -\hat{\mu} \,.\, \hat{\mathrm{H}} \qquad \rightarrow (1)$$

- Here $\hat{\mu}$ is the magnetic moment of the atom. It is proportional to the total angular momentum $\hbar\hat{J}$ of the atom and is conventionally written is the form

$$\hat{\mu} = g\mu_0\hat{J} \qquad \rightarrow \quad (2)$$

$$\mu_0 \ - magnetic\ moment\ \left[usually\ Bhor\ magnetic\ \mu_0 = \frac{e\hbar}{2mc}\right].$$

$$g \ - g\ factor\ of\ the\ atom.$$

By combining (1) and (2) one obtains

$$\epsilon = -g\ \mu_0\,\bar{J}\,.\,\bar{H} \ = -g\mu_0 HJ \qquad \rightarrow \quad (3)$$

Since $\widehat{H}$ points in the z-direction. In a quantum mechanical description the values which J_z can assume are discrete and are given by

$$J_Z = m$$

Where m can take on all values between $-J \; and +J$ in integral steps (i.e.,)

$$m = -J, -J+1, -J+2, \ldots J-1, J \quad \rightarrow (4)$$

$(2J+1)$ possible values of m corresponding to that many possible projections of the angular momentum vector along the z-axis.

So the possible magnetic energies of the atom are then

$$\epsilon_m = -g\mu_0 H m \quad \rightarrow (5)$$

The probability P_m that an atom is in a state labeled as ‘m’ is given by

$$P_m \infty \, e^{-\beta\varepsilon_m} = e^{\beta g\mu_0 H m}$$

The z component of its magnetic moment in this state is by (2) , equal to

$$\mu_z = g\mu_0 m$$

The mean z component of the magnetic moment of an atom is therefore

$$\overline{\mu_z} = \sum x_i \;\; p_i$$

$$\overline{\mu_z} = \frac{\sum_{m=-J}^{J} e^{\beta g\mu_0 H m}(g\mu_0 m)}{\sum_{m=-J}^{J} e^{\beta g\mu_0 H m}}$$

The numerator can conveniently be written as a derivative w.r.to the external parameter H, that is

$$\sum_{m=-J}^{J} e^{\beta g \mu_0 H m} (g\mu_0 m) = \frac{1}{\beta}\frac{dZ}{dH}$$

$$where\ Z = \sum_{m=-J}^{J} e^{\beta g \mu_0 H m} \quad \rightarrow (7)$$

↓ Partition function of one atom.

Hence (6) becomes

$$\bar{\mu}_z = \frac{1}{\beta}\frac{1}{z}\frac{\partial z}{\partial H} = \frac{1}{\beta}\frac{\partial \log z}{\partial H} \quad \rightarrow (8)$$

To calculate z, let us introduce the abbreviation

$$\eta = \beta g \mu_0 H = \frac{g\mu_0 H}{KT} \quad \rightarrow (9)$$

which is a dimensionless parameter which measures the ratio of the magnetic energy $g\mu_0 H$ to thermal energy KT.

$$z = \sum_{m=-J}^{J} e^{\eta m} = e^{-nJ} + e^{-n(J-1)} + \cdots + e^{nJ}$$

which is simply a finite geometric series where each term is obtained from the preceding one as a result of multiplication by e^{η}. This can immediately be summed to give

$$z = \frac{e^{-nJ} - e^{n(J+1)}}{1 - e^{\eta}}$$

$$\sum_{n=-3}^{3} e^{an} = e^{-3a} + e^{-2a} + e^{-a} + 1 + e^{a} + e^{2a} + e^{3a} = \frac{e^{-3a} - e^{4a}}{(1 - e^{a})}$$

$$\frac{e^{-3a} - e^{4a}}{(1 - e^{a})} = (e^{-3a} - e^{4a})(1 + e^{a} + e^{2a} + e^{3a} + e^{4a} + e^{5a} + e^{6a} + \cdots)$$

$$= e^{-3a} + e^{-2a} + e^{-a} + 1 + e^{a} + e^{2a} + e^{3a} + e^{4a} + e^{5a} + e^{6a} + \cdots$$

$$-e^{4a} - e^{5a} - e^{6a} - \cdots$$

$$= e^{-3a} + e^{-2a} + e^{-a} + 1 + e^{a} + e^{2a} + e^{3a}$$

This can be brought to more symmetrical form by multiplying both numerator and denominator by $e^{-\frac{\eta}{2}}$.

Then

$$z = \frac{e^{-\eta\left(J+\frac{1}{2}\right)} - e^{\eta\left(J+\frac{1}{2}\right)}}{e^{-\frac{\eta}{2}} - e^{\frac{\eta}{2}}}$$

(or)

$$z = \frac{\sinh\left(J+\frac{1}{2}\right)\eta}{\sinh\frac{\eta}{2}} \quad \rightarrow (11)$$

$$\log z = \log\sinh\left(J+\frac{1}{2}\right)\eta - \log\sinh\frac{\eta}{2} \quad \rightarrow (12)$$

$$\mu = \frac{1}{\beta}\frac{\partial \log z}{\partial H} = \frac{1}{\beta}\frac{\partial \log z}{\partial \eta}\frac{\partial \eta}{\partial H} = g\mu_0\frac{\partial \log z}{\partial \eta} \qquad \rightarrow (10)$$

Substituting (12) into (10)

$$\mu_+ = g\mu_0\left[\frac{\left(J+\frac{1}{2}\right)\cosh\left(J+\frac{1}{2}\right)\eta}{\sinh\left(J+\frac{1}{2}\right)\eta} - \frac{\frac{1}{2}\cosh\frac{\eta}{2}}{\sinh\frac{\eta}{2}}\right]$$

(or)

$$\mu_z = g\mu_0 J \, . B_J(\eta) \quad \rightarrow (13)$$

$$B_J(\eta) = \frac{1}{J}\left[\left(J+\frac{1}{2}\right)\coth\left(J+\frac{1}{2}\right)\eta - \frac{1}{2}\coth\frac{\eta}{2}\right] \qquad \rightarrow (14)$$

Sometimes called “ Brillouin function”.

Paramagnetism:

If there are N_o atoms per unit volume, the mean magnetic moment per unit volume (or magnetization) becomes

$$M_z = N_0\,\bar{\mu}_z = N_0 g\mu_0 J B_J(\eta)$$

Limiting cases: CASE 1:

$$\eta \gg 1, \qquad that\ is \quad \frac{g\mu_0 H}{KT} \gg 1$$

$M_z \rightarrow N_0 g\mu_0 J$ (goes to a constant level).

Explanation

$$We\ know\ \coth y = \frac{\cosh y}{\sinh y} = \frac{e^y + e^{-y}}{e^y - e^{-y}}$$

$y \gg 1$, both $e^{-y} \ll e^y$ so coth y = 1

So that

$$B_J(\eta) = \frac{1}{J}\left[\left(J + \frac{1}{2}\right)\coth\left(J + \frac{1}{2}\right)\eta - \frac{1}{2}\coth\frac{1}{2}\eta\right] = \frac{1}{J}\left[\left(J + \frac{1}{2}\right) - \frac{1}{2}\right] = 1$$

$$M = N_0 g\mu_0 J \qquad \rightarrow (A)$$

Limiting cases: CASE 2:

$y \ll 1$, both e^y and e^{-y} can be expanded in power series retaining all terms quadratic in y, the result is

$$\coth y = \frac{\left(1 + y + \frac{y^2}{2}\right) + \left(1 - y + \frac{y^2}{2}\right)}{\left(1 + y + \frac{y^2}{2} + \frac{y^3}{6}\right) - \left(1 - y + \frac{y^2}{2} - \frac{y^3}{6}\right)}$$

$$= \frac{2 + y^2}{2y + \frac{2y^3}{3}} = \frac{2\left(1 + \frac{y^2}{2}\right)}{2\left(y + \frac{y^3}{6}\right)} = \frac{1 + \frac{y^2}{2} + \cdots}{y + \frac{1}{6}y^3 + ..}$$

$$= \left(1 + \frac{y^2}{2}\right)\left[\frac{1}{y}\left(1 + \frac{y^2}{6}\right)^{-1}\right] = \frac{1}{y}\left(1 + \frac{y^2}{2}\right)\left(1 - \frac{y^2}{6}\right)$$

$$\coth y = \left(\frac{1}{y} + \frac{y}{3}\right) \qquad y \ll 1$$

$$B_J(\eta) = \frac{1}{J}\left\{\left(J+\frac{1}{2}\right)\left[\frac{1}{\left(J+\frac{1}{2}\right)\eta} + \frac{1}{3}\left(J+\frac{1}{2}\right)\eta\right] - \frac{1}{2}\left[\frac{2}{\eta}+\frac{\eta}{6}\right]\right\}$$

$$= \frac{1}{J}\left\{\frac{1}{3}\left(J+\frac{1}{2}\right)^2\eta - \frac{\eta}{12}\right\} = \frac{\eta}{3J}\left\{J^2 + J + \frac{1}{4} - \frac{1}{4}\right\} = \frac{(J+1)}{3}\eta$$

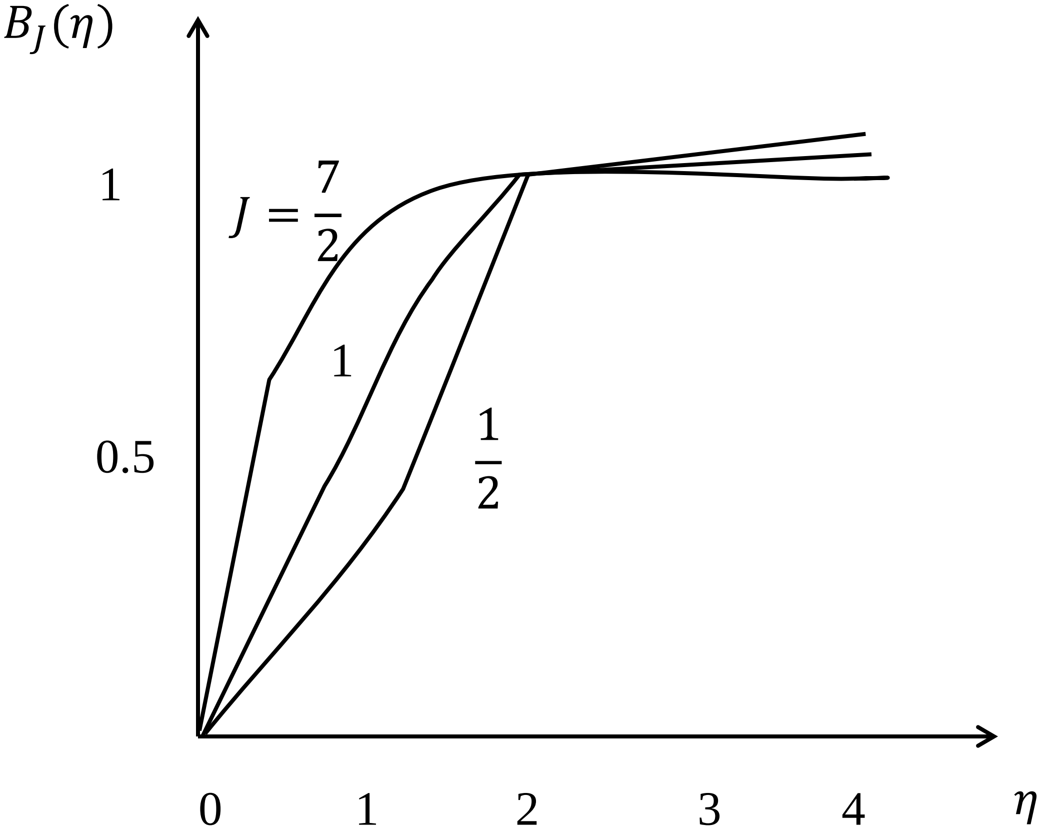
$$\therefore \eta \ll 1 \qquad \overline{M_z} = N_0 g\mu\, J\ \frac{(J+1)}{3}\eta \propto \ \eta \propto \frac{H}{T}$$

$$\therefore M_z = \chi H$$

$$Susceptibility = \frac{N_0 g^2 \mu_0^2 J(J+1)}{3KT}$$

$\chi \propto T^{-1}$ → *Known as Curic law*

Dependence of the Brillouin function $B_J(\eta)$ $on\ u_n$ argument η for various values of J



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