Magnetism

If a particle having a magnetic moment $\boldsymbol{\mu}$ is placed in a magnetic field **B,** its energy is given by :

$$E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B \text{ (If } \mathbf{B} \text{ is in the z-direction).}$$

Let us first find a method for calculating the average of μ_z. If μ_z takes a value μ_i in the i-th state of the particle, its Partition Function will be given by :

$$z = \Sigma_i \exp(+\beta\mu_i B)$$

$$\Rightarrow \quad \partial(\ln z)/\partial B = (1/z)\,\partial z/\partial B = \Sigma_i\, \beta\mu_i \exp(+\beta\mu_i B)/z$$

$$\Rightarrow \quad \mathbf{(1/\beta)\,\partial(\ln z)/\partial B} = \Sigma_i\, \mu_i \exp(+\beta\mu_i B)/z$$

$$= \Sigma_i\, \mu_i \exp(-\beta E_i)/\Sigma_i \exp(-\beta E_i)$$

$$= \langle\mu\rangle$$

The above equation is a key result in the theory of magnetism.

Langevin Problem

This problem deals with a paramagnetic substance, with the molecules having an **intrinsic magnetic dipole moment m**, placed in an external magnetic field **B**. Classically, the dipoles can be oriented in any direction in space. (No space quantization). If we chose our z-axis in the direction of the magnetic field, a small solid angle with the tail of the dipole as origin, is given by :

$$d\omega = dS/r^2 = \sin\theta\, d\theta\, d\phi.$$

Theoretically, there are **infinite** number of possible directions, *even* within this small solid angle. However, we assume that the number of possible orientations of the dipole within this solid angle is **proportional** to the solid angle. Each orientation defines a state of the dipoles (apart from its other parameters, like position, momentum, etc.) Therefore the no. of states within $d\omega$ is :

$$A\, d\omega = A \sin\theta\, d\theta\, d\phi.$$

The energy of a magnetic dipole **m** in a magnetic field **B** is given by :

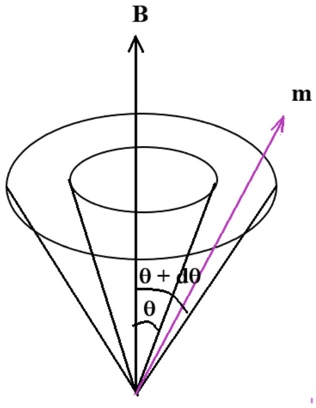
$$E = -\mathbf{m}\cdot\mathbf{B} = -mB\cos\theta.$$

Therefore, each of the above states have energy. Thus the Partition Function is given by :

$$z = \int A \sin\theta\, d\theta\, d\phi\, e^{+\beta mB\cos\theta},$$

where the sum over states has become an integral. Integrating over 'ϕ' :

$$z = A\int 2\pi \sin\theta\, d\theta\, e^{\beta mB\cos\theta}.$$



[Actually, $2\pi \sin\theta\, d\theta$ gives the solid angle generated by two cones with semi-vertical angles θ and $\theta + d\theta$, with the tail of the dipole as origin. So, the no. of states within **this** solid angle = $2\pi A \sin\theta\, d\theta$.]

Substitute : $\beta mB\cos\theta = u \Rightarrow du = -\beta mB \sin\theta\, d\theta$

If $\theta = 0$, $u = \beta mB$ and if $\theta = \pi$, $u = -\beta mB$

$\Rightarrow$ $\mathbf{z} = -(2\pi A/\beta mB)\int e^u\, du$ [within the limits βmB and $-\beta mB$]

$$= +\mathbf{(2\pi A/\beta mB)\,[e^{\beta mB} - e^{-\beta mB}] = 4\pi A \sinh(\beta mB)/\beta mB},$$

since, $\sinh x = (e^x - e^{-x})/2$.

Now, in general, the Partition Function for a magnetic dipole, placed in a magnetic field in the z-direction is given by : $z = \Sigma\, e^{+\beta mB\cos\theta}$. Therefore, the average magnetic moment in the z-direction : $\mathbf{\langle m_z\rangle = \langle m\cos\theta\rangle = (1/\beta)\,\partial(\ln z)/\partial B}$.

In this case, $\ln z = \ln(4\pi A) + \ln \sinh(\beta mB) - \ln(\beta mB)$

$$\Rightarrow \langle m_z \rangle = m\,[\,\coth(\beta m B) - 1/(\beta m B)\,].$$

The function : $[\coth(x) - 1/x]$ is called the **Langevin function**.

Low Temp / Strong field limit :

If $T \to 0$, or equivalently, $B \to \infty$, $x = (mB/KT) \to \infty$

$$\Rightarrow e^{mB/KT} \to \infty,\ e^{-mB/KT} \to 0,$$

$$\Rightarrow \coth(mB/KT) = (e^{mB/KT} + e^{-mB/KT}) / (e^{mB/KT} - e^{-mB/KT})$$

$$\approx e^{mB/KT} / e^{mB/KT} = 1$$

and $1/x = (KT/MB) \to 0$.

$$\Rightarrow \langle m_z \rangle \to m$$

This means, all the dipoles are oriented along the magnetic field (magnetic saturation).

High Temp / Weak field limit :

If $T \to \infty$, or equivalently, $B \to 0$, $x = (mB/KT) \to 0$

$$\Rightarrow e^{x} \approx 1 + x + x^2/2 + x^3/6,\ e^{-x} \approx 1 - x + x^2/2 - x^3/6,$$

$$\Rightarrow (e^{x} + e^{-x}) / (e^{x} - e^{-x}) \approx (1 + x^2/2) / (x + x^3/6)$$

$$\approx (1 + x^2/2)/x \times [1 + x^2/6]^{-1}$$

$$\approx (1/x + x/2) \times [1 - x^2/6]$$

$$\approx (1/x + x/2 - x/6) \approx (1/x + x/3)$$

- Check that, if you approximate : $e^{x} \approx 1 + x$ and $e^{-x} \approx 1 - x$, coth x would cancel 1/x and you would get a zero result.
- if you approximate : $e^{x} \approx 1 + x + x^2/2$ and $e^{-x} \approx 1 - x + x^2/2$, you would miss a contribution $O(x)$, if get a wrong coefficient of x.

$\Rightarrow [\coth x - 1/x] \approx x/3$, which $\to 0$ **linearly** as $x = (mB/KT) \to 0$

$$\Rightarrow \langle m_z \rangle \approx \mathbf{m\,(mB/3KT)}.$$

For 'N' molecules per unit volume, the **intensity of magnetization** (dipole moment / unit volume)

$$\approx Nm^2B/3KT$$

and the **magnetic susceptibility** χ (intensity of magnetization / unit magnetizing field)

$$\approx Nm^2/3KT.$$

Thus, $\chi \propto 1/T$, which nothing but **Curie's law**.

Pauli spin para-magnetism problem

(A free spin - ½ particle, (e^-) in a constant magnetic field (a Quantum Theory)

If a particle has an angular momentum **j**, it will have a magnetic moment

$$\boldsymbol{\mu} = g\,\mu_B\,\mathbf{j},$$

where 'g' is the Lande g-factor (which equals 2 for a free electron) and 'μ_B' is the **Bohr Magneton**, which equals ($e\hbar/2m$). Hence,

$$E = -\mu_z B = -g\mu_B j_z B.$$

For a free spin-½ particle, $j_z = \pm ½$

$$\Rightarrow\ E = -2 \times \mu_B \times (\pm ½)\, B = -\mu_B B, \text{ or } +\mu_B B$$

$$\Rightarrow\ z = \Sigma_i \exp(-\beta E_i) = \mathbf{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} \quad \text{————— (7)}$$

$$= 2\cosh(\beta\mu_B B), \text{ since } \cosh x = (e^{x} + e^{-x})/2$$

<u>Avg. energy per particle :</u>

$$\langle E\rangle = -\partial\, \ln z/\partial\beta = -(1/z)\, \partial z/\partial\beta$$

$$z = (e^{\beta\mu_B B} + e^{-\beta\mu_B B})$$

$$\Rightarrow \langle E\rangle = -\mu_B B\, (e^{\beta\mu_B B} - e^{-\beta\mu_B B}) / (e^{\beta\mu_B B} + e^{-\beta\mu_B B}) \quad \text{———— (8)}$$

$$= -\mu_B B \tanh(\beta\mu_B B)$$

<u>Avg. magnetic moment per particle along z :</u>

$$z = 2\cosh(\beta\mu_B B), \quad \text{[from eq.(6)]}$$

$$\Rightarrow \langle\mu\rangle = (1/\beta)\, \partial(\ln z)/\partial B = (1/z)\, \partial z/\partial B$$

$$= \mu_B \sinh(\beta\mu_B B) / \cosh(\beta\mu_B B) = \boldsymbol{\mu_B \tanh(\beta\mu_B B)} \quad \text{———— (9)}$$

For N non-interacting (or rather 'weakly interacting') spins, the N-particle Partition Function :

$$Z_N = z^N, \text{ where } z = e^{\beta\mu_B B} + e^{-\beta\mu_B B} \quad \text{[from eq.(6)]}$$

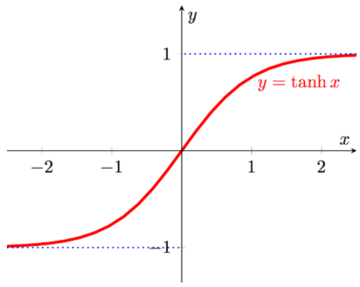
$$\Rightarrow \langle E\rangle = -\partial \ln Z_N/\partial\beta = -N\, \partial(\ln z)/\partial\beta$$

$$= -N \mu_B B \tanh(\beta\mu_B B),$$

which is just N-times the avg. single particle energy.

Similarly, $\langle\mu\rangle = (1/\beta)\, \partial(\ln z)/\partial B = N \mu_B \tanh(\beta\mu_B B)$,

which is again, N-times the avg. magnetic moment per particle.



As $B \to \infty$ (strong magnetic field) or $\beta \to \infty$ $(T \to 0)$,

$$\exp(-\beta\mu_i B) \to 0 \Rightarrow \tanh(\beta\mu_B B) = (e^{\beta\mu_B B} - e^{-\beta\mu_B B}) / (e^{\beta\mu_B B} + e^{-\beta\mu_B B})$$

$$\to 1$$

$$\Rightarrow \langle\mu\rangle \to \mu_B$$

This signifies magnetic saturation. (All the dipoles are oriented in the direction of the magnetic field.

<u>Partition Function for N free spin - ½ particle in a constant magnetic field :</u>

If we wish to calculate the N-particle partition (Z_N) *directly*, for this problem, we obtain the same result (z^N), but in a non-trivial way.

In the N-particle system, if 'n' number of spins point upward and (N – n) spins downward, then the total energy becomes :

$$\mathbf{E = -n\, \mu_B B + (N - n)\, \mu_B B}$$

The number ways we can choose the n up-spins out of N is : ${}^{N}C_n$, which is the degeneracy of the above energy value.

Hence the Partition Function :

$$Z_N = \Sigma\, {}^{N}C_n\, e^{-\beta\{-n\,\mu B\, B + (N-n)\, \mu B\, B\}}$$

$$= \Sigma\, {}^{N}C_n\, [e^{+\beta\, \mu B\, B}]^n\, [e^{-\beta\, \mu B\, B}]^{(N-n)}$$

This is clearly, a binomial expansion, leading to the simplification :

$$Z_N = [e^{+\beta\, \mu B\, B} + e^{-\beta\, \mu B\, B}]^N = z^N,$$

where 'z' is the single-particle Partition Function, as expected.

<u>Brillouin (ব্রিলওঁয়া) Problem</u>

This problem deals with a paramagnetic substance, with the molecules having an angular momentum **J** and hence, a magnetic dipole moment $\mathbf{m} = \mathbf{g}\, \mathbf{m_B}\, \mathbf{J}$, where **J** is the resultant of orbital angular momentum (**L**) and spin (**S**), 'g' is the so-called gyromagnetic ratio and m_B (= $e\hbar/2m$) is the Bohr magneton.

The molecules are placed in an external magnetic field **B**. Classically, the dipoles can be oriented in any direction in space. However, according to Quantum Mechanics, their orientation must be such that 'J_z' can take (2J + 1) values : + J to – J in steps of '1'. If we chose our z-axis in the direction of the magnetic field, the energy of a magnetic dipole **m** is given by :

$$E = -\mathbf{m}\cdot\mathbf{B} = -\, m_z B = -\, g m_B JB,\ -\, g m_B (J-1)B, \cdots + g m_B JB.$$

$$= -\,xJ,\ -\,x(J-1), \cdots + xJ, \text{ where } \mathbf{x = g m_B B}.$$

(Text books often define x = **$gm_B BJ$**)

The Partition Function therefore equals :

$$z = \exp(-\beta x J) + \exp(-\beta x J + \beta x) + \exp(-\beta x J + 2\beta x) + \cdots + \exp(+\beta x J)$$

This is a GP series, with the **1st term (a) = exp(– βx J)**, **common ratio (r) = exp(βx)** and **no. of terms (n) = (2J + 1)**.

Hence, $z = \mathbf{a\,(r^n - 1)/(r - 1)} = \exp(-\beta xJ) \times [\exp\{\beta x(2J+1)\} - 1] / [\exp(\beta x) - 1]$

$$= [\exp\{\beta x(J+1)\} - \exp(-\beta x J)] / [\exp(\beta x) - 1].$$

Let us pull out a factor **exp{ βx /2}** as common, both from the numerator and the denominator.

$$\Rightarrow z = [\exp\{\beta x(J+\tfrac{1}{2})\} - \exp(-\beta x(J+\tfrac{1}{2})] / [\exp(\beta x/2) - \exp(-\beta x/2)]$$

$$= \mathbf{\sinh\{\beta x(J+\tfrac{1}{2})\} / \sinh\{\beta x/2\}}.$$

The average magnetic moment in the z-direction :

$$\langle \mathbf{m_z} \rangle = \mathbf{(1/\beta)\, \partial (\ln z)/\partial B}$$

$$\Rightarrow \langle \mathbf{m_z} \rangle = \mathbf{g m_B [(J+\tfrac{1}{2}) \coth\{\beta x(J+\tfrac{1}{2})\} - \tfrac{1}{2}\coth\{\beta x/2\}]}$$

The function : $[(J+\tfrac{1}{2}) \coth\{\beta x(J+\tfrac{1}{2})\} - \tfrac{1}{2}\, g m_B \coth\{\beta x/2\}]$ is called the **Brillouin Function**.

[The usual definition is : $[(2J+1)/2J \coth\{\beta x(2J+1)/2J\} - 1/2J\, g m_B \coth\{\beta x/2J\}$, with x = **$gm_B BJ$**. In that case, $\langle \mathbf{m_z} \rangle = \mathbf{g m_B J B_J(x)}$]

<u>Low Temp / Strong field limit :</u>

If $T \to 0$, or equivalently, $B \to \infty$, $\beta x = (\beta g m_B B) \to \infty$

Now, as $y \to \infty$, $e^{-y} \to 0 \Rightarrow \coth(y) = (e^y + e^{-y}) / (e^y - e^{-y}) \to 1$.

$\Rightarrow \coth\{\beta x(J+\tfrac{1}{2})\}$ and $\coth\{\beta x/2\} \to 1$.

$\Rightarrow \langle \mathbf{m_z} \rangle \to \mathbf{g m_B [(J+\tfrac{1}{2}) - \tfrac{1}{2}] = g m_B J}$,

This means, each dipole is oriented along the magnetic field (Jz = J, m_z = gm_B J).

<u>High Temp / Weak field limit :</u>

If $T \to \infty$, or equivalently, $B \to 0$, $\beta x = (\beta g m_B B) \to 0$

$\coth(y) = (e^{y} + e^{-y})/(e^{y} - e^{-y}) = (1 + y^2/2 + \text{- - -})/(y + y^3/6 + \text{- - -})$

$= (1 + y^2/2 + \text{- - -}/y)\ [1 + y^2/6 + \text{- - -}]^{-1}$

$= (1 + y^2/2 + \text{- - -}/y)\ [1 - y^2/6 + \text{- - -}]$

$\approx (1 + y^2/3 + \text{- - -}/y) \approx 1/y + y/3$

$\Rightarrow B_J(x) \approx (J + ½)/\ [1/\beta x(J + ½) + (J + ½)\beta x/3] - ½\ [2/\beta x + \beta x/6]$

= ~~$1/\beta x$~~ $+ (J + ½)^2\ \beta x/3 -$ ~~$1/\beta x$~~ $- \beta x/12$

$= (4J^2 + 4J)\ \beta x/12$

$= J(J + 1)\ \beta x/3$

$\Rightarrow \langle m_z\rangle \rightarrow g m_B\, J(J + 1)\ \beta x/3 \quad = \quad g^2 m_B^2\, B\ J(J+1)/3KT.$

- Take J = ½ and calculate z and $\langle m_z\rangle$. Check that the results match with those for Pauli Spin Paramagnetism.

<u>Classical Limit</u>

Note that if J is large, the separation between the successive m_J's ($\Delta m_J = 1$) becomes small compared to the total angular momentum, which means that the angular momentum vector may make almost all possible angles with the z-axis. Note also, that $g m_B J = m$, which is the magnetic moment of a single dipole. Thus, $\langle m_z\rangle \rightarrow$ **$(m/J)^2 B\ J(J+1)/3KT \rightarrow m^2 B/3KT$, which is the Langevin limit.**

<u>Ferro-magnetism</u>

Weiss' Mean Field Theory :

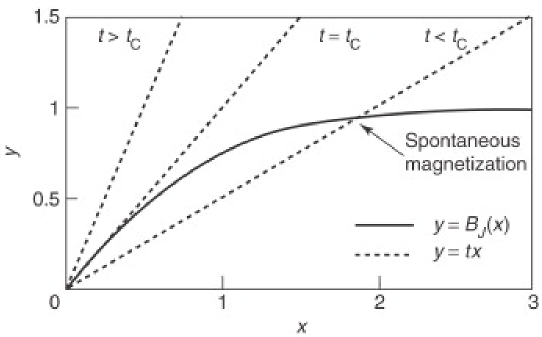
Weiss suggested that the dipoles within a material, if aligned at least partially, will produce a magnetic field, **apart from the magnetic field (B_{ex}) applied externally**. This field will be proportional to the intensity of magnetisation (**M**) at that particular stage and may be expressed as : (λ**M**). The total field : **B** = (**B_{ex}** + λ**M**) will be responsible for aligning the dipoles.
Substituting in the Brillouin theory :

$M = N\ g\ \mu_B\ J\ B_J(x)$, where $B_J(x)$ is the Brillouin function and $x = (g\ \mu_B J\ B/KT)$

B is now equal to ($B_{ex} + \lambda M$). Thus the above equation contains M both in the left hand and the right hand side. We must look for a self consistent solution for M, i.e. the total magnetic field B, which depends on the magnetization M, should produce the same value for M.
In particular, if the external field B_{ex} is switched off, it will be interesting to find whether any non-zero solution for M is available, i.e., whether the internal field produced by the dipoles themselves can maintain their alignment. If available, we call it 'spontaneous magnetization'.
In this situation :

$$M = N\ g\ \mu_B\ J\ B_J(x), \text{ ---- (1)}$$

where $x = g\ \mu_B J\ \lambda M/KT$ (since $B_{ex} = 0$) $\Rightarrow M = KT\ x/(g\mu_B J\ \lambda)$ ---- (2)



We plot both expressions for M against x and find the graphical solution.
As the temperature increases, the slope of the second curve (straight line) increases. At some stage it becomes tangential to the first curve (which is essentially the plot of the Brillouin function) at the origin. This is the highest temperature at which spontaneous magnetization is possible. After that, we do not have any intersection of the two curves except at x = 0.

Now, $B_J(x) = (2J + 1)/2J\ [\coth\{(2J + 1)x/2J\}] - (1/2J)\ [\coth(x/2J)]$

Near $x = 0$,

$\coth(x) = (e^x + e^{-x})/(e^x - e^{-x}) = (1 + x^2/2 + - - -) / (x + x^3/6 + - - -)$

$= (1 + x^2/2 + - - - / x) [1 + x^2/6 + - - -]^{-1}$

$= (1 + x^2/2 + - - - / x) [1 - x^2/6 + - - -]$

$\approx (1 + x^2/3 + - - - /x) \approx 1/x + x/3$

$\Rightarrow B_J(x) \approx (2J + 1)/2J [2J /(2J + 1)x + (2J + 1)x/6J] - (1/2J) [2J/x + x/6J]$

$= x + (2J + 1)^2 x/12J^2 - x - x/12J^2$

$= (4J^2 + 4J) x/12J^2$

$= (J + 1) x/3J$ ---- (3)

The gradient of the tangent to the M vs. x curve, as obtained from (1) is given by :

$dM/dx = Ng\mu_B J\, dB_J/dx$,

Near $x = 0$, $dB_J/dx \approx (J + 1)/3J$ [from (3)] $\Rightarrow dM/dx = Ng\mu_B (J +1)/3$ ---- (4)

The gradient of the M vs. x straight line curve, as obtained from (2) = $KT / (g\mu_B J \lambda)$ ---- (5)

If this exceeds or equals the gradient (4), no non-zero solution for M exists. Thus, the condition for obtaining a non-trivial solution is :

$KT/ (g\mu_B J \lambda) \le Ng\mu_B (J +1)/ 3$ $\Rightarrow$ The critical temperature, above which there will no spontaneous magnetization is :

$$\mathbf{T = Ng^2\mu_B^2 J(J +1)\lambda/ 3K}.$$

(Also known as the Curie Temperature).

Currie-Weiss Law

If both the external and the internal fields are present,

$M = Ng\mu_B JB_J(x) \approx Ng\mu_B(J + 1) x/3J$ [from eq.(3)]

$= Ng\mu_B(J + 1) /3 \times g\mu_B J (B_{ex} + \lambda M)/KT$

$= Ng^2\mu_B^2 J(J + 1) /3KT \times (B_{ex} + \lambda M) = \alpha/T \times (B_{ex} + \lambda M)$,

where $\alpha = Ng^2\mu_B^2 J(J + 1) /3K$

$\Rightarrow M [1 - \alpha \lambda/T] = \alpha B_{ex}/T \Rightarrow M [T - \alpha \lambda] = \alpha B_{ex}$

$\Rightarrow M = \alpha B_{ex} /[T - \alpha \lambda]$

$\Rightarrow \boldsymbol{\chi = M /H = \mu_0 M/B = \mu_0\alpha /[T - \alpha \lambda]}$

This is Currie-Weiss Law, where $T_C = \alpha\lambda = Ng^2\mu_B^2 J(J + 1) \lambda/3K$

Ferro-magnetism from Langevin Theory

According to Langevin theory, $M = Nm\, L(x)$, where 'N' is the number of molecules per unit volume, 'm' is the dipole moment of each individual moelecule and L(x) is he Langevin function of $x = mB/KT$.

Following the approach by Weiss, we replace B by $(B_{ex} + \lambda M)$, where λM is the internal field due to the molecular dipoles. Thus, 'M' now appears on both sides of the above equation. We must find a self consistent solution for M.

In particular, if the external field B_{ex} is switched off, it will be interesting to find whether any non-zero solution for M is available, i.e., whether the internal field produced by the dipoles themselves can maintain their alignment. If available, we call it 'spontaneous magnetization'.

In this situation :

$M = Nm\, L(x)$, ---- (1)

where $x = m (\lambda M)/KT$ (since $B_{ex} = 0$) $\Rightarrow M = KT\, x/\lambda m$ ---- (2)

We can plot both expressions for M against x and find the graphical solution. (

As the temperature increases, the slope of the second curve (straight line) increases. At some stage it becomes tangential to the first curve at the origin. (See the figure in the Brillouin theory for Ferro-magnetism).This is the highest temperature at which spontaneous magnetization is possible. After that, we do not have any intersection of the two curves except at x = 0.

If $T \to \infty$, or equivalently, $B \to 0$, $x = (mB/KT) \to 0$

$\Rightarrow\ e^x \approx 1 + x + x^2/2 + x^3/6,\ e^{-x} \approx 1 - x + x^2/2 - x^3/6$,

$\Rightarrow\ (e^x + e^{-x}) / (e^x - e^{-x}) \approx (1 + x^2/2) / (x + x^3/6)$

$\approx (1 + x^2/2)/x \times [1 + x^2/6]^{-1}$

$\approx (1/x + x/2) \times [1 - x^2/6]$

$\approx (1/x + x/2 - x/6) \approx (1/x + x/3)$

$\Rightarrow$ **L(x) = coth(x) – 1/x** $\approx x/3$

Thus the gradient of the first curve dM/dx = Nm dL/dx near origin = Nm/3, which is to be equated with that of the second curve KT/ λm. $\Rightarrow$ Nm/3 = KT/λm

$\Rightarrow$ **T = $Nm^2\lambda/3K$**