Statistics of Paramagnetism (Chapter 17)

The most famous types of Magnetic materials are:

(i) *Paramagnetic*: A property exhibit by substances which, when placed in a magnetic field, are magnetized parallel to the field to an extent proportional to the field (except at very low temperatures or in extremely large magnetic fields).

(ii) *Ferromagnetic*: A property, exhibited by certain materials, alloys, and compound of the transition (iron group), rare-earth, and actinide elements, in which the internal magnetic moments spontaneously organized in a common direction; gives rise to a permeability considerably greater than that of vacuum, and to magnetic hysteresis.

(iii) *Diamagnetic*: Having a magnetic permeability less than one; materials with this property are repelled by a magnet and tend to position themselves at right angles to magnetic lines of force.

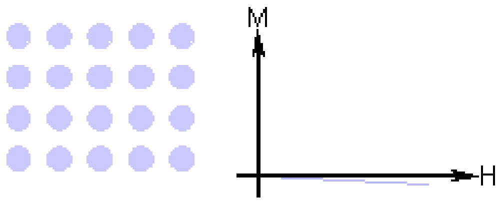
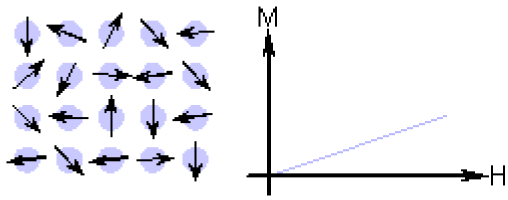
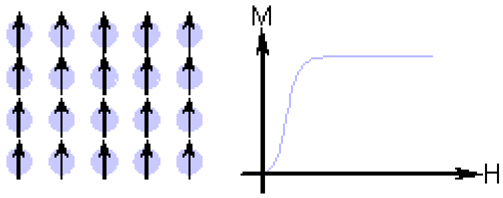
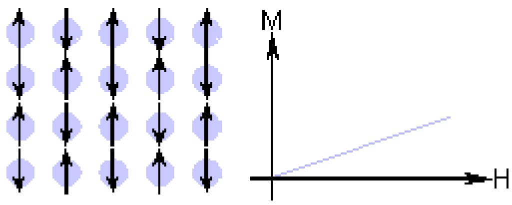
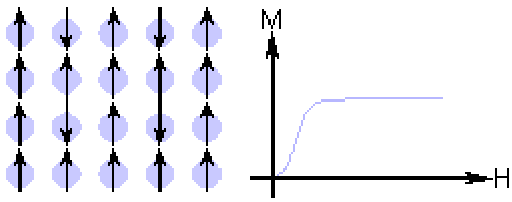
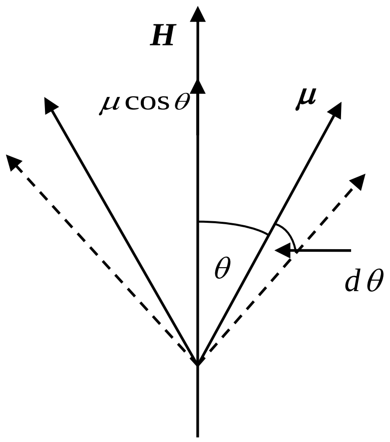
Type of Magnetism	***Susceptibility***	***Atomic / Magnetic Behaviour***		***Example / Susceptibility***
Diamagnetism	Small & negative.	Atoms have no magnetic moment		Au -2.74x10^{-6} Cu -0.77x10^{-6}
Paramagnetism	Small & positive.	Atoms have randomly oriented magnetic moments		β-Sn 00.19x10^{-6} Pt 21.04x10^{-6} Mn 66.10x10^{-6}
Ferromagnetism	Large & positive, function of applied field, microstructure dependent.	Atoms have parallel aligned magnetic moments		Fe ~100,000
Antiferromagnetism	Small & positive.	Atoms have mixed parallel and anti-parallel aligned magnetic moments		Cr 3.6x10^{-6}
Ferrimagnetism	Large & positive, function of applied field, microstructure dependent	Atoms have anti-parallel aligned magnetic moments		Ba ferrite ~3

Table 1 Summary of different types of magnetic behavior.

Magnetic susceptibility χ represents the response of a system to the external field.
Hysteresis means the dependence of the polarization of ferromagnetic materials not only on the applied (magnetic) field but also on their previous history.
Magnetic domain, a region of ferromagnetic material within which atomic or molecular magnetic moments are aligned parallel.
Permeability, a factor, characteristic of a material, that is proportional to the magnetic induction produced in a material divided by the magnetic field strength; it is a tensor when these quantities are not parallel.
Consult Phys-102 book for more details discussion.

Model: Consider N identical, localized (i.e. distinguishable), practically static, mutually noninteracting and freely orientable dipoles at absolute temperature T and placed in an external magnetic field H pointing along z direction. Then the torque acting on the dipole is given by: $\bar{\tau} = \bar{\mu} \times \bar{H} = \mu H \sin\theta$, and the (magnetic) potential energy can be written as: $\varepsilon = -\bar{\mu}.\bar{H} = -\mu H \cos\theta$, where θ is the angle between the magnetic field and the dipole and μ is the magnetic dipole moment.



$$\varepsilon = \int_{\pi/2}^{\theta} \tau d\theta = \mu H \int_{\pi/2}^{\theta} \sin\theta d\theta = -\mu H \cos\theta = -\boldsymbol{\mu} \bullet \boldsymbol{H} = \mu_z H,$$

1- Qualitative Description:
A non-interacting atom with magnetic dipole moment μ (μ is positive) could be point either parallel or anti-parallel to an external magnetic field H. At temperature T, we have the question:

Q: What is the mean magnetic moment $\bar{\mu}_H$ (in the direction H) of such an atom?
A: There are two possible states, and they are:

state	condition	Magnetic energy	probability
(+)	$\mu \uparrow H \uparrow$	$\varepsilon_+ = -\mu H$ (lower $\bar{\mu}_H = \mu$)	$P_+ = Ce^{\beta\mu H}$
(-)	$\mu \downarrow H \uparrow$	$\varepsilon_- = \mu H$ (higher $\bar{\mu}_H = \mu$)	$P_- = Ce^{-\beta\mu H}$

ε_+ is lower energy	$\Rightarrow$	atom is more likely to be found
ε_- is higher energy	$\Rightarrow$	atom is less likely to be found

Define

$$\eta = \beta\mu H = \frac{\mu H}{k_B T} = \frac{\text{Magnetic energy}}{\text{Thermal energy}}$$

η is a dimensionless parameter which measure the ratio of the magnetic energy μH , which tends to align the magnetic moment, to the thermal energy $k_B T$, which tends to keep it randomly oriented. Then

Case 1	$\eta << 1$	$T >> 1$ $H << 1$	$P_+ = P_-$	$\bar{\mu}_H = 0 \Rightarrow \mu$ is randomly oriented (disorder)
Case 2	$\eta >> 1$	$T << 1$ $H >> 1$	$P_+ = 1,\ P_- = 0$	$\bar{\mu}_H = \mu \Rightarrow \mu \uparrow H \uparrow$ (ordered)

1- Qualitative Description: (17.3)

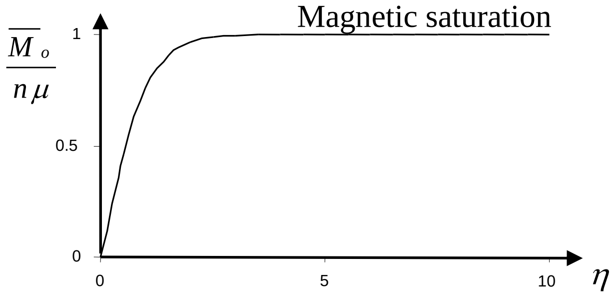
The mean magnetic moment $\bar{\mu}_H$ is given by:

$$\bar{\mu}_H = \frac{\mu P_+ + (-\mu) P_-}{P_+ + P_-} = \mu \frac{e^{\eta} - e^{-\eta}}{e^{\eta} + e^{-\eta}} = \mu \tanh \eta$$

The ''magnetization'' $\bar{M}_o$, or mean magnetic moment per unit volume, is then in the direction of H and reads

$$\bar{M}_o = n\bar{\mu}_H = \begin{cases} n\mu\eta = \chi H & \text{for } \eta \ll 1 \text{ (high temperature)} \\ n\mu & \text{for } \eta \gg 1 \text{ (low temperature)} \end{cases}$$

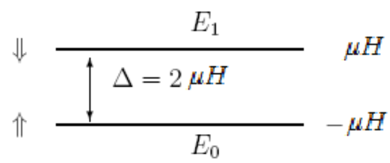
where n is the total number of magnetic atoms per unit volume. The above results agree with the qualitative descriptions. Here, $\chi = \frac{n\mu^2}{k_B T}$ is the "magnetic susceptibility". The result $\chi \propto \frac{1}{T}$ is known as **Curie's law**. At very low temperature $\bar{M}_o$ becomes independent of H and equal to the maximum (or "saturation magnetization") magnetization which the substance can exhibit. Saturation magnetization means complete alignment of the magnetic dipoles in the field direction.



T large, high disorder T small, low disorder H larger → more ordered

Figure: Total magnetic moment of a spin ½ paramagnet.

Example: A N-monatomic Boltzmann ideal gas of spin ½ atoms in a uniform magnetic field, in addition to its usual kinetic energy, a magnetic energy of $\varepsilon_1 = -\varepsilon$ and $\varepsilon_2 = \varepsilon$ per atom, $\varepsilon = \mu H$, where is the magnetic moment. (It is assumed that the gas is so dilute that the interaction of magnetic moments may be neglected.)



a- What is the partition function of the system?

$$z = e^{-\beta\varepsilon_1} + e^{\beta\varepsilon_2} = e^{-\eta} + e^{\eta} = 2\cosh(\eta), \qquad \eta = \beta\varepsilon$$

$$\bar{E} = \frac{1}{z}\left(\varepsilon_1 e^{-\beta\varepsilon_1} + \varepsilon_2 e^{\beta\varepsilon_2}\right) = \frac{\varepsilon e^{-\eta} - \varepsilon e^{\eta}}{2\cosh(\eta)} = -\varepsilon\tanh(\eta)$$

and the total energy $U = N\bar{E} = -N\varepsilon\tanh(\eta)$.

In summary:

Quantity	Formula
Partition function	$z = 2\cosh(\eta) \quad \Rightarrow \quad Z_N = 2^N \cosh^N(\eta)$
Helmholtz free energy	$F = -Nk_B T \ln(Z_N) = -Nk_B T \ln\{2\cosh(\eta)\}$
Entropy	$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B \ln\left[2\cosh(\eta) - \eta\tanh(\eta)\right]$

Internal energy	$U=-\left(\dfrac{\partial \ln Z}{\partial \beta}\right)_{V,N}=-N\,\mu H\,\tanh(\eta)$
Heat capacity	$C_H=\left(\dfrac{\partial U}{\partial T}\right)_H=-T\left(\dfrac{\partial^2 F}{\partial T^2}\right)_{V,N}=\dfrac{Nk_B\eta^2}{\cosh^2\eta}$
Total magnetic moment	$M=-\left(\dfrac{\partial F}{\partial H}\right)_{V,N}\;(=n\bar{\mu}=\dfrac{\mu e^{\eta}-\mu e^{-\eta}}{e^{\eta}+e^{-\eta}}=n\mu\tanh(\eta))$

Notice that: $U=-M\,\text{H}$

Figure: Heat capacity of spin ½ paramagnet. (Schottky anomaly)

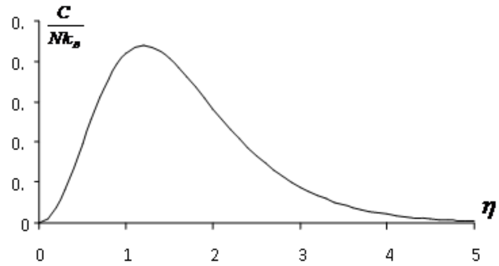
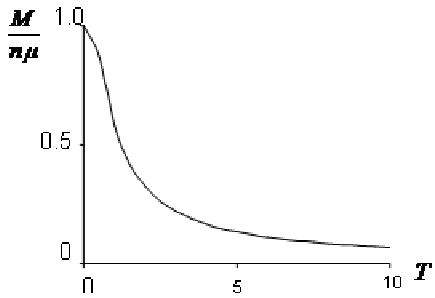
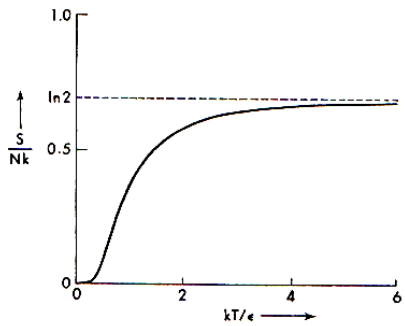
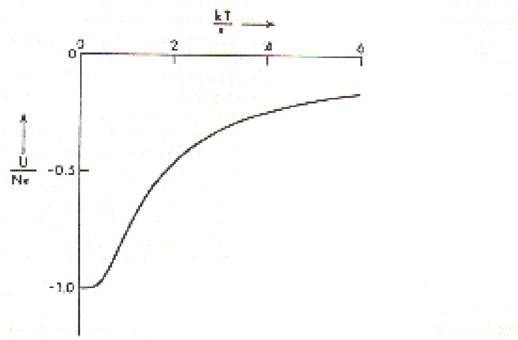


Figure: Total magnetic moment of a spin ½ paramagnet.





. The entropy of a system of magnetic dipoles (with $J=\frac{1}{2}$) as a function of temperature.



. The energy of a system of magnetic dipoles (with $J=\frac{1}{2}$) as a function of temperature.

Comments:

1- For the internal energy: At low T, all the spins are aligned with the field and the energy per spin is close to $-\mu H$. However as T increases, thermal fluctuations start to flip some of the spins; this is noticeable when $k_B T$ is of the order of μH. As T gets very large, the energy tends to zero as the number of up and down spins become more nearly equal. $\dfrac{P_-}{P_+}=Ce^{-2\beta\mu H}$, so it never exceeds one. We can say that: at high temperature, the thermal energy is sufficient to disorder the magnetic dipole orientation.

2- The heat capacity tends to zero both at high and low T . At low T the heat capacity is small because $k_B T$ is much smaller than the energy gap $2\mu H$, so thermal fluctuations which flip spins are rare and it is hard for the system to absorb heat. This behavior is universal; quantization means that there is always minimum excitation energy of a system and if the temperature is low enough, the system can no longer absorb heat. The high-T behavior arises because the number of down-spins never exceeds the number of up-spins, and the energy has a maximum of zero. As the temperature gets very high, that limit is close to being reached, and raising the temperature still further makes very little difference. For $\varepsilon/kT \sim 1.2$, the heat capacity has a fairly sharp peak known as a *Schottky anomaly*. The anomaly is useful for determining energy level splittings of ions in rare-earth and transition-group metals. This behavior is *not* universal, but only occurs where there is a finite number of energy levels (here, there are only two). Most systems have an infinite tower of energy levels, there is no maximum energy and the heat capacity does not fall off.

3- It is not easy to attain the maximum of the paramagnetic heat capacity curve as the following calculation shows. The paramagnetic heat capacity becomes important only at very low temperatures. The maximum occurs at $\eta \approx 1$, i.e. $\frac{\mu H}{k_B T} = 1$. Now the magnitude of

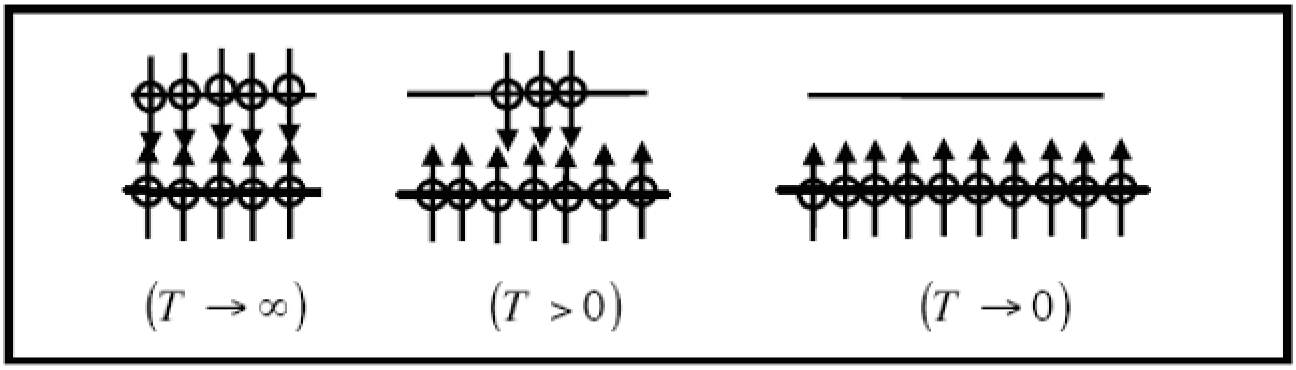
$$\frac{\mu}{k_B} = \frac{9.27\times10^{-24}}{1.38\times10^{-23}} \approx 1$$

so to get the maximum we must have $H \approx T_c$

maximum attainable fields are $H \approx 1$ Tesla

so we need a maximum temperature of $T_c \approx 1$ K

4- Like the energy, the heat capacity is qualitatively different from other systems in its variation with temperature. The most important thermodynamic property of two-level systems is the entropy.



5- At zero temperature, the magnetization goes to $N\mu$ and all the spins are up. There is an order, and so the entropy is zero. The stronger the field, the higher the temperature has to be before the spins start to be appreciably disordered. At high temperatures the spins are nearly as likely to be up as down; the magnetization falls to zero and the entropy reaches a maximum. The entropy of this state is $Nk_B \ln 2$. Remember that, 2 is the total number of microstates.

I- Quantum mechanical treatment of paramagnetic system

i. Review of ½ electron system

In ½ electron sytem, it was found that:

1- the single-particle partition function – the sum over the 2 possible energy states of a dipole as:

$$z=\sum \mathrm{e}^{-\beta\varepsilon}=\mathrm{e}^{\beta\mu B}+\mathrm{e}^{-\beta\mu B}=2\cosh\eta,$$

And $Z_N=z^N$

2- The free Helmholtz function

$$F=-N\,\mathrm{k_B}T\ln\cosh\eta-N\,\mathrm{k_B}T\ln 2$$

3- Magnetization

$$M=-\frac{1}{\mu_0}\left(\frac{\partial F}{\partial H}\right)_T=-\frac{1}{\mu_0}\left(\frac{\partial F}{\partial \eta}\right)_T\left(\frac{\partial \eta}{\partial H}\right)_T$$

$$=-\left(-N\,\mathrm{k_B}T\frac{\sinh\eta}{\cosh\eta}\right)\frac{\mu}{\mathrm{k_B}T}=\underline{\underline{N\mu\tanh\eta}}$$

4- Entropy

$$S=-\left(\frac{\partial F}{\partial T}\right)_H$$

$$=N\,\mathrm{k_B}\ln\cosh\eta+N\,\mathrm{k_B}T\tanh\eta\frac{\partial\eta}{\partial T}+N\,\mathrm{k_B}\ln 2$$

$$\frac{\partial x}{\partial T}=-\frac{\mu H}{\mathrm{k_B}T^2}$$

hence

$$\mathrm{S}=N\,\mathrm{k_B}\ln\cosh\eta-N\,\mathrm{k_B}T\frac{\mu H}{\mathrm{k_B}T^2}\tanh\eta+N\,\mathrm{k_B}\ln 2$$

$$=\underline{\underline{N\,\mathrm{k_B}\left(\ln 2+\ln\cosh\eta-\eta\tanh\eta\right)}}$$

The maximum value of $S/N\mathrm{k_B}=\ln 2$ because of the two possible dipole orientations, and occurs at $x=0$ which, it is easy to derive, implies complete disordering at high temperatures or at vanishing external field.

5- Internal energy

$$U=F+TS=-N\,\mathrm{k_B}T\ln\cosh\eta-N\,\mathrm{k_B}T\ln 2+N\,\mathrm{k_B}T\left(\ln 2+\ln\cosh\eta-\eta\tanh\eta\right)$$

$$=-N\,\mathrm{k_B}T\,\eta\tanh\eta=-N\mu H\tanh\eta\equiv\underline{\underline{-\mu MH}}$$

Or through the partion function as:

$$U=-\frac{\partial}{\partial\beta}\ln Z_N=-N\frac{\partial}{\partial\beta}\ln Z_1,\qquad \text{where } Z_1=2\cosh\eta$$

$$=\ -N\frac{\partial}{\partial\eta}\ln Z_1\left(\frac{\partial\eta}{\partial\beta}\right),$$

On differentiating we get $U=-N\tanh\eta\left(\mu H\right)$

$$=\underline{\underline{-N\mu H\tanh\eta}}\qquad\text{as before}$$

6- Heat capacity

$$C_H = \left(\frac{\partial U}{\partial T}\right)_H = T\left(\frac{\partial S}{\partial T}\right)_H \qquad \text{for reversible changes}$$

$$= T\left(\frac{\partial S}{\partial \eta}\right)_H \left(\frac{\partial \eta}{\partial T}\right)_H = TN\,\mathrm{k_B}\left(\frac{\partial}{\partial \eta}\ln\cosh\eta - \frac{\partial}{\partial x}\eta\tanh x\right)\left(-\frac{\mu H}{\mathrm{k_B}\,T^2}\right)$$

$$= -N\,\mathrm{k_B}\,\eta\left(\tanh\eta - \tanh\eta - \eta\,\mathrm{sech}^2\,\eta\right) = \underline{\underline{N\,\mathrm{k_B}\,\eta^2\,\mathrm{sech}^2\,\eta}}$$

الدوال الزائدية
Hyperbolic Functions

نتعامل بدراستنا بدوال مثلثية بالصورة:

$$\cos\theta=\frac{e^{i\theta}+e^{-i\theta}}{2},\quad \sin\theta=\frac{e^{i\theta}-e^{-i\theta}}{2i},\quad \tan\theta=\frac{\sin\theta}{\cos\theta} \qquad (1)$$

ومن المفيد أحياناً أن نستخدم صوراً أخرى للدوال مثل:

$$\sec\theta=\frac{1}{\cos\theta},\quad \mathrm{cosec}\theta=\frac{1}{\sin\theta},\quad \cot\theta=\frac{1}{\tan\theta} \qquad (2)$$

وفي دراستنا للفيزياء الإحصائية نتعامل مع دوال أخرى مثل الدوال المثلثة الزائدية والتي تعرف كالتالي:

$$\cosh\theta=\frac{e^{\theta}+e^{-\theta}}{2},\quad \sinh\theta=\frac{e^{\theta}-e^{-\theta}}{2},\quad \tanh\theta=\frac{\sinh\theta}{\cosh\theta} \qquad (3)$$

وأيضاً

$$\mathrm{sech}\theta=\frac{1}{\cosh\theta},\quad \mathrm{cosech}\theta=\frac{1}{\sinh\theta},\quad \coth\theta=\frac{1}{\tanh\theta} \qquad (4)$$

ومن التعريفات السابقة من السهل أن نستنتج التفاضلات:

$$\frac{d\cosh\theta}{d\theta}=\sinh\theta,\quad \frac{d\,\sinh\theta}{d\theta}=\cosh\theta,\quad \frac{d\,\tanh\theta}{d\theta}=\mathrm{sech}^2\theta \qquad (5)$$

وغالباً ما تظهر لنا القيم الفيزيائية، مثل دالة التجميع والطاقة الخ، في صور دوال معقدة من الصعب التعامل معها ودراستها. بالتالي فإن ما نصبو إليه هو البحث عن صيغة تقريبية ومبسطة للدالة المعقدة بحيث نستطيع دراسة خواص النظام. لذا فنحن نلجأ إلى دراسة القيم الفيزيائية عند حدود (قيم) المتغير θ الصغيرة والكبيرة لهذه الدوال. بالرغم من أننا نعلم أنه عندما $\theta\to 0$ فإن $\sinh\theta\to 0$، لكن هذا مالا نبحث عنه. ببساطة نحن نبحث عن سلوك الدالة عندما تقترب من الحدود.

ولقيم صغيرة من θ، نجد أنه باستخدام المفكوك $e^{\theta}=1+\theta+\frac{1}{2}\theta^2+\cdots$ نحصل على:

$$\sinh\theta\xrightarrow{\theta\to 0}\theta,\quad \tanh\theta\xrightarrow{\theta\to 0}\theta,\quad \cosh\theta\xrightarrow{x\to 0}1+\tfrac{1}{2}\theta^2 \qquad (6)$$

الحدود النهائية للدالة $\cosh\theta$ غالباً ما تسبب لنا بعض المشاكل، إن احتفظنا بحدود θ^2 اعتماداً على المشكلة الفيزيائية، فإننا نستطيع أن ننظر للحل عدما نقترب من الصفر أو مالانهاية. ومن المهم أن نتذكر التقريب:

$$\cosh\theta\xrightarrow{x\to 0}1 \quad \text{but} \quad \cosh\theta-1\xrightarrow{x\to 0}\tfrac{1}{2}\theta^2 \qquad (7)$$

هذا أيضاً ينطبق على المفكوك:

$$e^{\theta} \xrightarrow{x\to 0} 1 \qquad \text{but} \qquad e^{\theta}-1 \xrightarrow{x\to 0} \tfrac{1}{2}\theta^2 \tag{8}$$

كمثال نجد أنه في بعض المسائل المعينة نجد أن طاقة النظام هي:

$$\langle E\rangle = \frac{\hbar\omega}{e^{\hbar\omega\beta}-1} \tag{9}$$

فإذا استخدمنا بسذاجة التقريب للدالة $e^{\hbar\omega\beta}$ عند درجات الحرارة العليا، أي بمعنى أن $\beta \to 0$، نجد أن المقام يؤول للصفر وبالتالي فإن الطاقة تؤول إلى مالانهاية. ولكن إذا طورنا تفكيرنا فسوف نجد أن المقام يؤول إلى $\hbar\omega\beta$ وبالتالي نجد أن $\langle E\rangle = \frac{1}{\beta} = k_B T$. هذا التقريب تظهر أهميته حيث إنه يمكن التحقق منه عملياً.

عند الحدود العليا للمتغير θ، نجد أن $e^{-\theta} \to 0$ ولذا فإن:

$$\sinh\theta \xrightarrow{\theta\to\infty} \tfrac{1}{2}e^{\theta}, \qquad \cosh\theta \xrightarrow{\theta\to\infty} \tfrac{1}{2}e^{\theta},$$
$$\tanh\theta \xrightarrow{\theta\to 0} 0, \qquad \tanh\theta \xrightarrow{\theta\to\infty} 1 \tag{10}$$

مثال: أوجد مفكوك الدالة $\coth x$ إلى الحد x.

الحل: باستخدام المفكوك $e^x = 1 + x + \frac{1}{2}x^2 + \cdots$ نجد أن:

$$\coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}} = \frac{e^{2x}+1}{e^{2x}-1} \approx \frac{1+(2x)+\frac{1}{2!}(2x)^2+\cdots+1}{1+(2x)+\frac{1}{2!}(2x)^2+\frac{1}{3!}(2x)^3+\cdots-1}$$
$$= \frac{2+2x+2x^2+\cdots}{2x+2x^2+4x^3/3+\cdots} = \frac{1}{x}\left(1+x+x^2+\cdots\right)\left(1+x+\frac{2x^2}{3}+\cdots\right)^{-1}$$
$$= \frac{1}{x}\left(1+x+x^2+\cdots\right)\left(1-x+\frac{x^2}{3}+\cdots\right)$$
$$= \frac{1}{x}\left(1+x-x+x^2-x^2+\frac{x^2}{3}+\cdots\right)$$
$$= \frac{1}{x}\left(1+\frac{x^2}{3}+\cdots\right) = \frac{1}{x}+\frac{x}{3}$$
