PHYC - 505: Statistical Mechanics
Homework Assignment 1
Solutions

1. A magnetic field B is applied to a system of a large number N of noninteracting spins each of magnetic moment μ at temperature T. Calculate (display analytic expressions) and plot (not merely sketch, do this with some graphing package)

   (a) the magnetization as a function of T at two given values of B,

   (b) the magnetization as a function of B at two given values of T,

   (c) the heat capacity of the system as a function of temperature T for a given value of B.

   Do each of these in a 1-dimensional, 2-dimensional, and 3-dimensional systems, carefully watching differences if any. The first of these is the system treated in class. For all three you have to evaluate appropriate integrals if necessary and express in terms of special functions such as hyperbolic, Bessel, etc.

   The basis of all your calculations should be the Boltzmann weight $\exp(-E/kT)$ and the expression for the energy for a spin as $E = -\mu B \cos\theta$, where θ is the angle between the directions of spin moment and the magnetic field.

Mathematical Aside: Generally speaking, for a system described above in any dimension, the associated energy, E, as given in lecture, is

$$E = -\vec{\mu} \cdot \vec{B} = -\mu B \cos\theta$$

where θ is the angle between the direction of the spin moment and the applied magnetic field, B. The partition function for one of the spins is defined as

$$\mathcal{Z}_1 = \int g(E) \mathrm{e}^{-\beta E} dE = \int \tilde{g}(\theta) \mathrm{e}^{\beta \mu B \cos\theta} d\Omega$$

where $\tilde{g}(\theta)$ can be thought of as the weight of each state allowable in the system between a torus of radius θ and $\theta + d\theta$ for each of the N spins. In 1-D, 2-D, and 3-D, this would be defined as

$$\tilde{g}_{\text{1-D}}(\theta) d\Omega = (\delta(\theta) + \delta(\theta - \pi))\, d\theta, \qquad \tilde{g}_{\text{2-D}}(\theta) d\Omega = d\theta,$$

and

$$\tilde{g}_{\text{3-D}}(\theta) d\Omega = \sin\theta d\theta \int_0^{2\pi} d\phi = 2\pi \sin\theta d\theta,$$

respectively. The partition function of the system of N particles is then given as

$$\mathcal{Z} = \mathcal{Z}_1^N$$

(before the Gibbs remedy is applied to the system, where we divide by $N!$; here this correction is not important since the properties that are being calculated are not affected by that factor in the end and therefore the $N!$ factor will not be used in the rest of these solutions).

The average energy of the system can then be found by taking the negative derivative with respect to β of the partition function as follows

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln\mathcal{Z} = -\frac{N}{\mathcal{Z}_1}\frac{\partial\mathcal{Z}_1}{\partial\beta}$$

The average magnetization of the system can be found in as similar manner as

$$\langle M\rangle = \frac{\partial}{\partial\beta B}\ln\mathcal{Z} = \frac{N}{\mathcal{Z}_1}\frac{\partial\mathcal{Z}_1}{\partial\beta}$$

The heat capacity of the system can be found by taking the temperature derivative of the average energy

$$C = \frac{d\langle E\rangle}{dT} = \frac{\partial\langle E\rangle}{\partial\beta}\frac{\partial\beta}{\partial T} = -\frac{1}{k_BT^2}\frac{\partial\langle E\rangle}{\partial\beta}$$

1-D: (**Note:** This case of the problem will be solved in the manner done in class.) For a 1 dimensional system of N noninteracting particles in equilibrium at temperature, T, in a magnetic field, B, with magnetic moment, μ there are two possible energy spin states, $E_\uparrow$ and $E_\downarrow$. The probabilities of a spin being in either state are

$$\mathcal{P}(E_\uparrow) = \frac{\mathrm{e}^{-\beta E_\uparrow}}{\mathrm{e}^{-\beta E_\downarrow}+\mathrm{e}^{-\beta E_\uparrow}} \qquad \text{and} \qquad \mathcal{P}(E_\downarrow) = \frac{\mathrm{e}^{-\beta E_\downarrow}}{\mathrm{e}^{-\beta E_\downarrow}+\mathrm{e}^{-\beta E_\uparrow}}$$

where

$$E_\uparrow = -\mu B \qquad \text{and} \qquad E_\downarrow = \mu B,$$

are the two energy states, and $\beta = \frac{1}{k_BT}$.
The average magnetization for the total magnetization of the system, as given in class, is

$$\langle M\rangle = N_\uparrow\mu + N_\downarrow(-\mu) = \mu\left(N_\uparrow - N_\downarrow\right)$$

where

$$N_\uparrow = N\mathcal{P}(E_\uparrow) = \frac{N\mathrm{e}^{-\beta E_\uparrow}}{\mathrm{e}^{-\beta E_\downarrow}+\mathrm{e}^{-\beta E_\uparrow}} \qquad \text{and} \qquad N_\downarrow = N\mathcal{P}(E_\downarrow) = \frac{N\mathrm{e}^{-\beta E_\downarrow}}{\mathrm{e}^{-\beta E_\downarrow}+\mathrm{e}^{-\beta E_\uparrow}},$$

The average magnetization is then rewritten as

$$\begin{aligned}
\langle M\rangle = \langle N\mu\rangle &= \mu\left(N_\uparrow - N_\downarrow\right) \\
&= N\mu\left(\frac{\mathrm{e}^{-\beta E_\uparrow}}{\mathrm{e}^{-\beta E_\downarrow}+\mathrm{e}^{-\beta E_\uparrow}} - \frac{\mathrm{e}^{-\beta E_\downarrow}}{\mathrm{e}^{-\beta E_\downarrow}+\mathrm{e}^{-\beta E_\uparrow}}\right) \\
&= N\mu\frac{\mathrm{e}^{\beta\mu B}-\mathrm{e}^{-\beta\mu B}}{\mathrm{e}^{-\beta\mu B}+\mathrm{e}^{\beta\mu B}} \\
&= N\mu\tanh\left(\beta\mu B\right) \\
&= N\mu\tanh\left(\frac{\mu B}{k_BT}\right)
\end{aligned}$$

For very low temperatures, that is, for

$$\frac{\mu B}{k_BT} >> 1$$

the average magnetization becomes constant with respect to both temperature, T, and magnetic field, B, as the hyperbolic tangent approaches unity,

$$\lim_{\frac{\mu B}{k_BT}\to\infty}\langle M\rangle = \lim_{\frac{\mu B}{k_BT}\to\infty} N\mu\tanh\left(\frac{\mu B}{k_BT}\right) \to N\mu$$

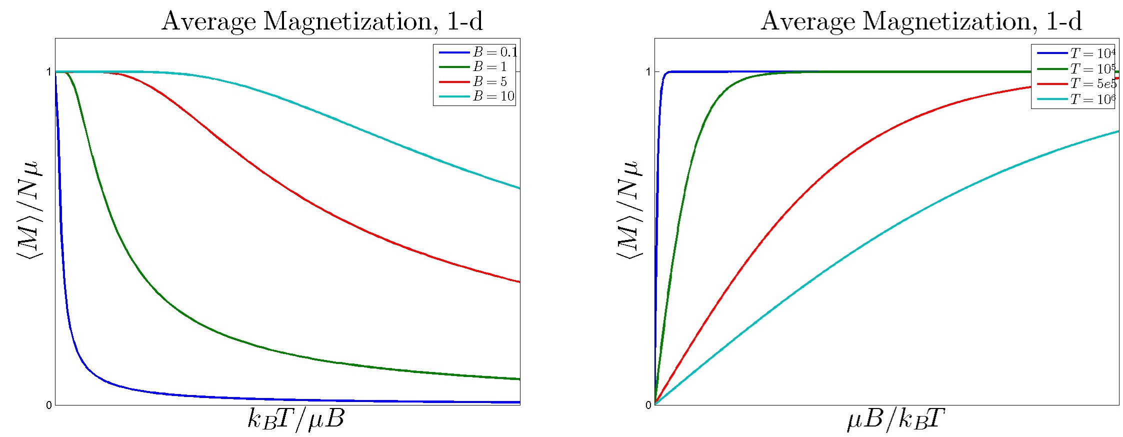


Figure 1. Here the fixed values of the magnetic field, B, and the temperature, T, are taken to be in arbitrary units.

whereas for very high temperatures, that is, for

$$\frac{\mu B}{k_B T} << 1$$

the hyperbolic tangent can be rewritten in terms of its Taylor series expansion, where

$$\tanh(x) = x - \frac{x^3}{3} + \cdots$$

and the average magnetization becomes

$$\lim_{\frac{\mu B}{k_B T} \to 0} \langle M \rangle = \lim_{\frac{\mu B}{k_B T} \to 0} N\mu \tanh\left(\frac{\mu B}{k_B T}\right) \to N\frac{\mu^2 B}{k_B T}$$

The heat capacity, C, is defined as the derivative of the average energy of all the spin states, $\langle E \rangle$, with respect to the temperature, T, as

$$C = \frac{d\langle E \rangle}{dT}$$

Now the average energy of this particular system in 1 dimension is defined (as in the notes)

$$\begin{aligned}
\langle E \rangle &= N_\uparrow E_\uparrow + N_\downarrow E_\downarrow \\
&= N\left((-\mu B)\frac{\mathrm{e}^{-\beta E_\uparrow}}{\mathrm{e}^{-\beta E_\downarrow} + \mathrm{e}^{-\beta E_\uparrow}} + \mu B\frac{\mathrm{e}^{-\beta E_\downarrow}}{\mathrm{e}^{-\beta E_\downarrow} + \mathrm{e}^{-\beta E_\uparrow}}\right) \\
&= -N\mu B\frac{\mathrm{e}^{\beta\mu B} - \mathrm{e}^{-\beta\mu B}}{\mathrm{e}^{-\beta\mu B} + \mathrm{e}^{\beta\mu B}} \\
&= -N\mu B \tanh\left(\beta\mu B\right) \\
&= -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right)
\end{aligned}$$

Taking the derivative with respect to the temperature of the above equation we have

$$\begin{aligned}
C = \frac{d\langle E \rangle}{dT} &= -N\mu B\frac{d}{dT}\left(\tanh\left(\frac{\mu B}{k_B T}\right)\right) \\
&= N\frac{\mu^2 B^2}{k_B T^2}\mathrm{sech}^2\left(\frac{\mu B}{k_B T}\right) \\
&= N k_B\left(\frac{\mu B}{k_B T}\right)^2 \mathrm{sech}^2\left(\frac{\mu B}{k_B T}\right)
\end{aligned}$$

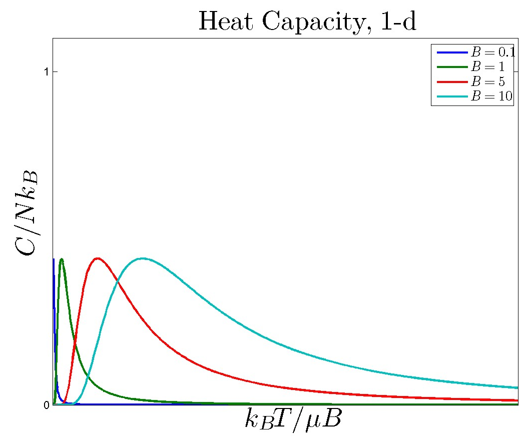


Figure 2. Here the fixed values of the magnetic field, B, are taken to be in arbitrary units.

For very low temperatures, that is, for

$$\frac{\mu B}{k_B T} >> 1$$

the heat capacity approaches zero

$$\lim_{\frac{\mu B}{k_B T}\to\infty} C = \lim_{\frac{\mu B}{k_B T}\to\infty} N k_B \left(\frac{\mu B}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\mu B}{k_B T}\right) \to 0$$

whereas for very high temperatures, that is, for

$$\frac{\mu B}{k_B T} << 1$$

the hyperbolic secant can be rewritten in terms of its Taylor series expansion, where

$$\operatorname{sech}^2(x) = \left(1 - \frac{x^2}{2} + \cdots\right)^2 = 1 - x^2 + \cdots$$

and the heat capacity becomes

$$\lim_{\frac{\mu B}{k_B T}\to 0} C = \lim_{\frac{\mu B}{k_B T}\to 0} N k_B \left(\frac{\mu B}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\mu B}{k_B T}\right) \to 0$$

2-D: Following from the mathematical aside above (or even from the lecture notes), we have that the partition function for this case is given as

$$\begin{aligned}\mathcal{Z} &= \mathcal{Z}_1^N \\ &= \left(\int_0^{2\pi} \mathrm{e}^{\beta\mu B\cos\theta} d\theta\right)^N\end{aligned}$$

This integral has the form of a modified Bessel function of the first kind of integral order $n = 0$

$$I_n(\beta\mu B) = \frac{1}{\pi}\int_0^{\pi} \mathrm{e}^{\beta\mu B\cos(u)}\cos(nu)\, du$$

Letting $u \to 2u$, and using the u-substitution that $\theta = 2u$, and $d\theta = 2du$, then we have the final form

$$I_n(\beta\mu B) = \frac{1}{2\pi}\int_0^{2\pi} \mathrm{e}^{\beta\mu B\cos(\theta)}\cos(n\theta)\, d\theta$$

yielding that the above integral for the partition function of the system is

$$\mathcal{Z} = (2\pi I_0(\beta\mu B))^N$$

The average energy is then

$$\begin{aligned}\langle E\rangle &= -\frac{N}{2\pi I_0(\beta\mu B)}\frac{\partial}{\partial\beta}(2\pi I_0(\beta\mu B)) \\ &= -N\mu B\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\end{aligned}$$

The average magnetization is found as

$$\begin{aligned}\langle M\rangle &= \frac{N}{2\pi I_0(\beta\mu B)}\frac{\partial}{\partial\beta B}(2\pi I_0(\beta\mu B)) \\ &= N\mu\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\end{aligned}$$

and the heat capacity is calculated as follows

$$\begin{aligned}C = \frac{d\langle E\rangle}{dT} &= -\frac{1}{k_BT^2}\frac{\partial\langle E\rangle}{\partial\beta} \\ &= -\frac{1}{k_BT^2}\frac{\partial}{\partial\beta}\left(-N\mu B\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\right) \\ &= \frac{N\mu B}{k_BT^2}\frac{\partial}{\partial\beta}\left(\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\right) \\ &= \frac{N\mu B}{k_BT^2}\left[-\mu B\left(\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\right)^2 + \frac{1}{I_0(\beta\mu B)}\frac{\partial I_1(\beta\mu B)}{\partial\beta}\right] \\ &= \frac{N\mu B}{k_BT^2}\left[-\mu B\left(\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\right)^2 + \frac{1}{I_0(\beta\mu B)}\left(\frac{\mu B}{2}(I_0(\beta\mu B) + I_2(\beta\mu B))\right)\right] \\ &= Nk_B\left(\frac{\mu B}{k_BT}\right)^2\left[-\left(\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\right)^2 + \frac{1}{2I_0(\beta\mu B)}(I_0(\beta\mu B) + I_2(\beta\mu B))\right] \\ &= Nk_B\left(\frac{\mu B}{k_BT}\right)^2\left[\frac{1}{2}\left(1 + \frac{I_2(\beta\mu B)}{I_0(\beta\mu B)}\right) - \left(\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\right)^2\right]\end{aligned}$$

For very low temperatures, that is, for

$$\beta\mu B >> 1$$

The Bessel functions approach each other, that is,

$$I_0(\beta\mu B) \sim I_1(\beta\mu B) \sim I_2(\beta\mu B)\cdots$$

as they grow exponentially toward infinity almost at the same rate, and therefore the average magnetization and heat capacity for $\beta\mu B \to \infty$ become

$$\lim_{\beta\mu B\to\infty}\langle M\rangle = \lim_{\beta\mu B\to\infty} N\mu\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)} \to N\mu$$

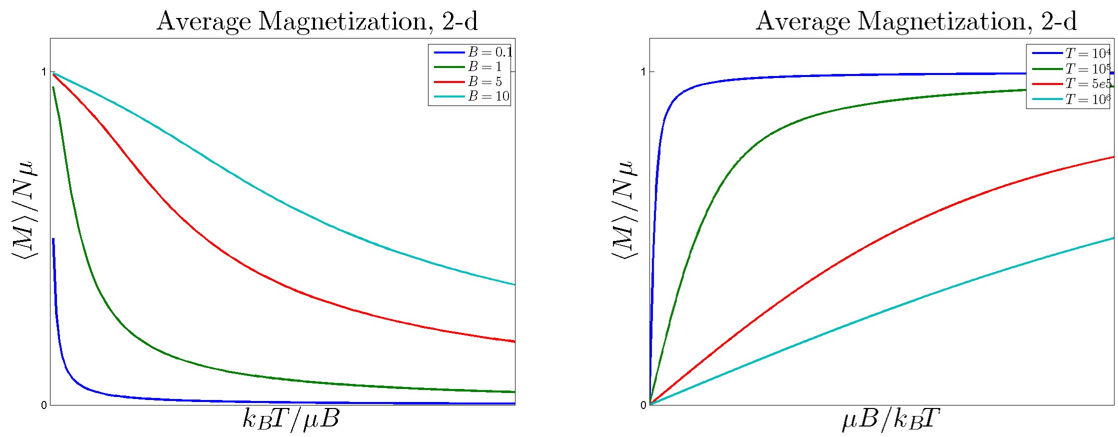


Figure 3. Here the fixed values of the magnetic field, B, and the temperature, T, are taken to be in arbitrary units.

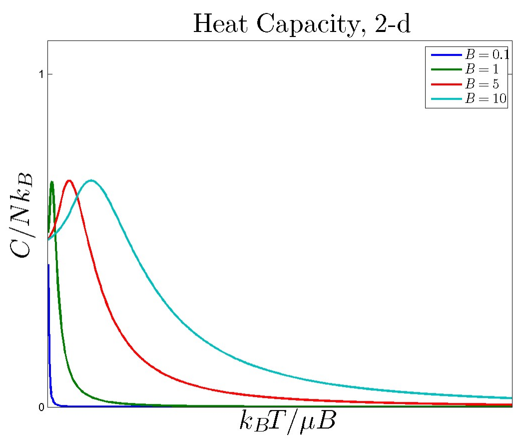


Figure 4. Here the fixed values of the magnetic field, B, are taken to be in arbitrary units.

and

$$
\begin{aligned}
\lim_{\beta\mu B\to\infty} C = Nk_B \lim_{\beta\mu B\to\infty} (\beta\mu B)^2 &\left[\frac{1}{2}\left(1+\frac{I_2(\beta\mu B)}{I_0(\beta\mu B)}\right) - \left(\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\right)^2\right] \\
&\to \frac{Nk_B}{2} \lim_{x\to\infty} \frac{x^2\left[I_0(x)^2 + I_2(x)I_0(x) - 2I_1(x)^2\right]}{I_0(x)^2} \\
&\overset{L'H}{=} \frac{Nk_B}{2} \lim_{x\to\infty} \left(\frac{2x\left[I_0(x)^2 + I_2(x)I_0(x) - 2I_1(x)^2\right]}{2I_0(x)I_1(x)}\right. \\
&\qquad \left. + \frac{x^2\left[2I_0(x)I_1(x) + I_2(x)I_1(x) + I_0(x)(I_1(x) - 2I_2(x)/x) - 2I_1(x)(I_0(x)+I_2(x))\right]}{2I_0(x)I_1(x)}\right) \\
&= \frac{Nk_B}{2} \lim_{x\to\infty} \left(\frac{x\left[I_0(x)^2 + I_2(x)I_0(x) - 2I_1(x)^2\right]}{I_0(x)I_1(x)}\right. \\
&\qquad\qquad \left. + \frac{x^2\left[I_0(x)(I_1(x) - 2I_2(x)/x) - I_1(x)I_2(x)\right]}{2I_0(x)I_1(x)}\right) \\
&= \frac{Nk_B}{2} \lim_{x\to\infty} \left(\frac{xI_0(x)}{I_1(x)} - 2\frac{xI_1(x)}{I_0(x)} + \frac{x^2\left[I_0(x)I_1(x) - I_1(x)I_2(x)\right]}{2I_0(x)I_1(x)}\right) \\
&\overset{L'H}{\cdots} \quad \vdots \\
&\to \frac{Nk_B}{2}
\end{aligned}
$$

respectively, whereas for very high temperatures, that is, for

$$\beta\mu B << 1$$

the average magnetization and heat capacity for $\beta\mu B \to 0$ become

$$\lim_{\beta\mu B\to 0} \langle M\rangle = \lim_{\beta\mu B\to 0} N\mu \frac{I_1(\beta\mu B)}{I_0(\beta\mu B)} \to N\mu\frac{0}{1} = 0$$

and

$$\begin{aligned}
\lim_{\beta\mu B\to 0} C &= \lim_{\beta\mu B\to 0} Nk_B\left(\beta\mu B\right)^2\left[\frac{1}{2}\left(1+\frac{I_2(\beta\mu B)}{I_0(\beta\mu B)}\right)-\left(\frac{I_1(\beta\mu B)}{I_0(\beta\mu B)}\right)^2\right] \\
&\to \lim_{\beta\mu B\to 0} Nk_B\left(\beta\mu B\right)^2\left[\frac{1}{2}\left(1+\frac{0}{1}\right)-\left(\frac{0}{1}\right)^2\right] \\
&= \lim_{\beta\mu B\to 0} \frac{Nk_B}{2}\left(\beta\mu B\right)^2 \to 0
\end{aligned}$$

3-D: Again, following from the mathematical aside above (or even from the lecture notes), we have that the partition function for this case is given as

$$\begin{aligned}
\mathcal{Z} &= \mathcal{Z}_1^N \\
&= \left(2\pi\int_0^\pi \mathrm{e}^{\beta\mu B\cos\theta}\sin\theta d\theta\right)^N \\
&= \left(-2\pi\int_1^{-1} \mathrm{e}^{\beta\mu B u} du\right)^N \\
&= \left[-2\pi\frac{1}{\beta\mu B}\left(\mathrm{e}^{-\beta\mu B}-\mathrm{e}^{\beta\mu B}\right)\right]^N \\
&= \left[\frac{2\pi}{\beta\mu B}\left(\mathrm{e}^{\beta\mu B}-\mathrm{e}^{-\beta\mu B}\right)\right]^N \\
&= \left[\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\right]^N
\end{aligned}$$

The average energy is then

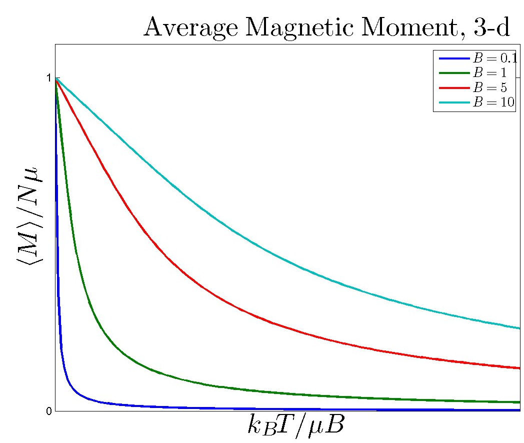
$$\begin{aligned}
\langle E\rangle &= -\frac{N}{\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)}\frac{\partial}{\partial\beta}\left(\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\right) \\
&= -\frac{N}{\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)}\left[-\frac{4\pi}{\beta^2\mu B}\sinh(\beta\mu B)+\frac{4\pi}{\beta}\cosh(\beta\mu B)\right] \\
&= -\frac{N}{\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)}\left[-\frac{4\pi}{\beta^2\mu B}\sinh(\beta\mu B)+\frac{4\pi}{\beta}\cosh(\beta\mu B)\right] \\
&= N\left[\frac{1}{\beta}-\mu B\coth(\beta\mu B)\right]
\end{aligned}$$

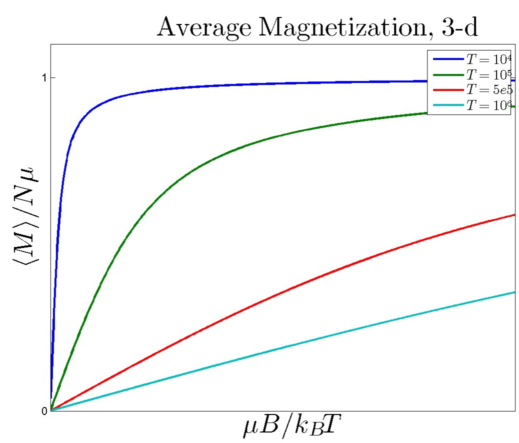
The average magnetization is found as

$$\begin{aligned}
\langle M\rangle &= \frac{N}{\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)}\frac{\partial}{\partial(\beta B)}\left(\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\right)\\
&= \frac{N}{\frac{4\pi}{\beta\mu}\sinh(\beta\mu B)}\frac{\partial}{\partial\beta}\left(\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\right)\\
&= \frac{N}{\frac{4\pi}{\beta\mu}\sinh(\beta\mu B)}\left[-\frac{4\pi}{\beta^2\mu B}\sinh(\beta\mu B)+\frac{4\pi}{\beta}\cosh(\beta\mu B)\right]\\
&= N\left[-\frac{1}{\beta B}+\mu\coth(\beta\mu B)\right]\\
&= N\mu\left[\coth(\beta\mu B)-\frac{1}{\beta\mu B}\right]
\end{aligned}$$

and the heat capacity is calculated as follows

$$\begin{aligned}
C = \frac{d\langle E\rangle}{dT} &= -\frac{1}{k_BT^2}\frac{\partial\langle E\rangle}{\partial\beta}\\
&= -\frac{1}{k_BT^2}\frac{\partial}{\partial\beta}\left(N\left[\frac{1}{\beta}-\mu B\coth(\beta\mu B)\right]\right)\\
&= -\frac{N}{k_BT^2}\left[-\frac{1}{\beta^2}+\mu^2B^2\mathrm{csch}^2(\beta\mu B)\right]\\
&= Nk_B\left[1-(\beta\mu B)^2\mathrm{csch}^2(\beta\mu B)\right]
\end{aligned}$$





For very low temperatures, that is, for

$$\beta\mu B >> 1$$

the average magnetization and heat capacity for $\beta\mu B\to\infty$ become

$$\lim_{\frac{\mu B}{k_BT}\to\infty}\langle M\rangle = \lim_{\frac{\mu B}{k_BT}\to\infty} N\mu\left[\coth(\beta\mu B)-\frac{1}{\beta B}\right]\to N\mu$$

and

$$\lim_{\frac{\mu B}{k_BT}\to\infty} C = \lim_{\frac{\mu B}{k_BT}\to\infty} Nk_B\left[1-(\beta\mu B)^2\mathrm{csch}^2(\beta\mu B)\right]\to Nk_B$$

respectively, whereas for very high temperatures, that is, for

$$\frac{\mu B}{k_BT} << 1$$

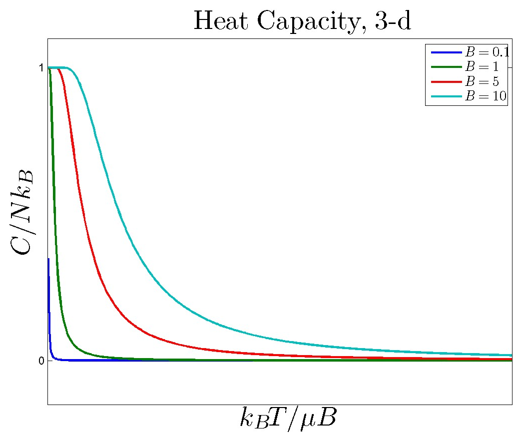


Figure 5. Here the fixed values of the magnetic field, B, and the temperature, T, are taken to be in arbitrary units.

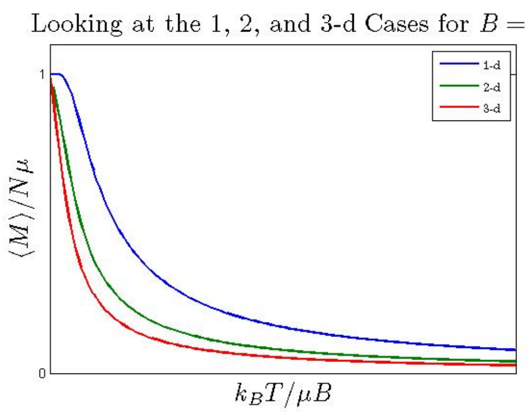
the average magnetization and heat capacity for $\beta\mu B \to 0$ become

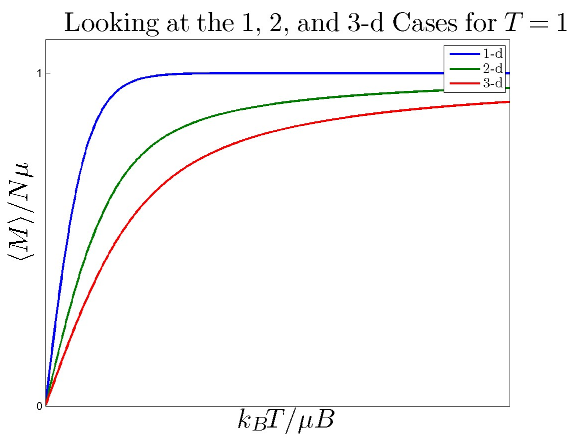
$$\lim_{\frac{\mu B}{k_B T}\to 0} \langle M\rangle = \lim_{\frac{\mu B}{k_B T}\to 0} N\mu \left[\coth(\beta\mu B) - \frac{1}{\beta B}\right] \to 0$$

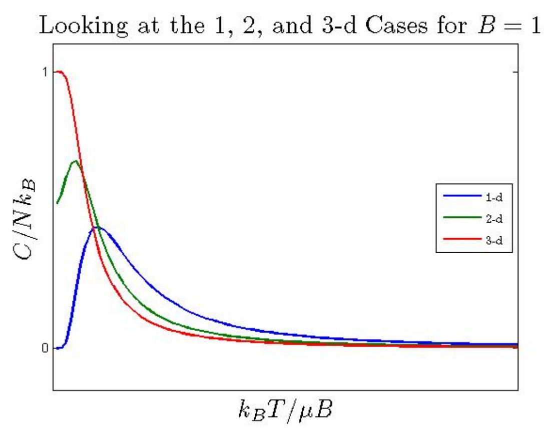
and

$$\lim_{\frac{\mu B}{k_B T}\to 0} C = \lim_{\frac{\mu B}{k_B T}\to 0} Nk_B \left[1 - (\beta\mu B)^2 \text{csch}^2(\beta\mu B)\right] \to 0$$

Looking at the plots for 1, 2, and 3 dimensions of the average magnetization and heat capacities we notice that the 2-d magnetization saturates to the maximum value of $N\mu$ slower than the 1-d case, but faster than the 3-d case. This happens because of the existence of allowed states that have energies between the extreme values of $\pm\mu B$. Compared to the 1-d case, these states contribute less to the magnetization than a completely aligned state, but are relatively more probable than a completely anti-aligned state. In the 3-d case, there are even more of these in-between states allowed since for any angle θ the spin can rotate around the B-field without changing its energy.







2. Read up from elementary books of your choice on thermodynamics, write down the first law of thermodynamics, and explain what you understand by entropy, free energy, and chemical potential. The answer should be not more than half a page.

The first law of thermodynamics states that the change of internal energy, ΔU, for a closed system that is taken from an initial to a final state of internal thermodynamic equilibrium, through an arbitrary process, is due to a combination of the heat added to the system, Q, and the work done by the system, W, yielding an equation of

$$\Delta U = Q - W$$

This is yet another form of the law of conservation of energy for a thermodynamic process consisting of an isolated system that is brought from one state to another, as the total energy remains constant.

Entropy is typically thought of as a measure of the disorder of a system, or as a measure of the number of ways in which a thermodynamic system can be arranged; however, in the case of the first law of thermodynamics, entropy is something that is produced in irreversible processes, such as Joule heating, diffusion, chemical reactions, etc., and, in its differential form, the first law of thermodynamics can be converted to the second law as

$$dU = \delta Q - PdV = TdS - PdV$$

where the total amount of heat added to a closed system is expressed as $\delta Q = TdS$, and S is the entropy of the system. Even though there is still conservation of energy for an isolated system, if it is undergoing an irreversible process, the entropy increase results from a generalized displacement in the system's conservation of energy, as the energy that is lost to heat cannot be converted to work, allowing the system to spontaneously move toward thermodynamic equilibrium at maximum entropy.

Free energy (Gibbs, Helmholtz, etc.) in the case of a thermodynamics is the amount of work that a thermodynamic system can perform in chemical or thermal processes in thermodynamic equilibrium. In terms of the first law of thermodynamics, for an isolated system, it is the change in internal energy minus the amount of energy that cannot be used to perform work.

The chemical potential, μ, is a form of potential energy per particle in a thermodynamic process that is released or absorbed during a chemical reaction in which a particle is removed from or added to or vice-versa a system. It is the Gibbs free energy per particle.