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4.5 Show that expression (4.3.20) **for the entropy of a system in the grand canonical ensemble can also be written as**

$$S = k\left[\frac{\partial}{\partial T}(Tq)\right]_{\mu,V}$$

Starting from equation (4.3.20) in the book.

$$S = kT\left(\frac{\partial q}{\partial T}\right)_{z,V} - Nk\ln z + kq \tag{1}$$

$$S = k\left[T\left(\frac{\partial q}{\partial T}\right)_{z,V} - N\ln z + q\right] \tag{2}$$

Substitute in for z in the above expression.

$$z = e^{\mu/kT} \tag{3}$$

$$S = k\left[T\left(\frac{\partial q}{\partial T}\right)_{z,V} - N\ln\exp\left(\mu/kT\right) + q\right] \tag{4}$$

$$S = k\left[T\left(\frac{\partial q}{\partial T}\right)_{z,V} - \frac{N\mu}{kT} + q\right] \tag{5}$$

Now relate $\left(\frac{\partial q}{\partial T}\right)_{z,V}$ to $\left(\frac{\partial q}{\partial T}\right)_{\mu,V}$ starting from the definition of q. Starting from equation (4.3.13), we know that:

$$q \equiv \ln\left[\sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)\right] \tag{6}$$

Find $\left(\frac{\partial q}{\partial T}\right)_{z,V}$.

$$\left(\frac{\partial q}{\partial T}\right)_{z,V} = \frac{\partial}{\partial T}\left(\ln\sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)\right)_{z,V} \tag{7}$$

$$\left(\frac{\partial q}{\partial T}\right)_{z,V} = \frac{1}{\sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)}\frac{\partial}{\partial T}\left(\sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)\right)_{z,V} \tag{8}$$

$$\left(\frac{\partial q}{\partial T}\right)_{z,V} = \frac{1}{\sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)}\sum_{N_r=0}^{\infty} z^{N_r}\frac{\partial Q_{N_r}(V,T)}{\partial T} \tag{9}$$

$$\left(\frac{\partial q}{\partial T}\right)_{z,V} = \sum_{N_r=0}^{\infty}\frac{z^{N_r}}{z^{N_r} Q_{N_r}(V,T)}\frac{\partial Q_{N_r}(V,T)}{\partial T} \tag{10}$$

$$\left(\frac{\partial q}{\partial T}\right)_{z,V} = \sum_{N_r=0}^{\infty}\frac{1}{Q_{N_r}(V,T)}\frac{\partial Q_{N_r}(V,T)}{\partial T} \tag{11}$$

Now find $\left(\frac{\partial q}{\partial T}\right)_{\mu,T}$.

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \frac{\partial}{\partial T}\left(\ln \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)\right)_{\mu,V} \tag{12}$$

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \frac{1}{\sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)} \frac{\partial}{\partial T}\left(\sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)\right)_{\mu,V} \tag{13}$$

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \frac{1}{\sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)} \sum_{N_r=0}^{\infty} z^{N_r} \frac{\partial Q_{N_r}(V,T)}{\partial T} + N_r z^{N_r-1}\left(\frac{\partial z}{\partial T}\right)_{\mu,V} Q_{N_r}(V,T) \tag{14}$$

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \sum_{N_r=0}^{\infty} \frac{z^{N_r} \frac{\partial Q_{N_r}(V,T)}{\partial T} + N_r z^{N_r-1}\left(\frac{\partial z}{\partial T}\right)_{\mu,V} Q_{N_r}(V,T)}{z^{N_r} Q_{N_r}(V,T)} \tag{15}$$

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \sum_{N_r=0}^{\infty} \frac{z^{N_r}}{z^{N_r} Q_{N_r}(V,T)} \frac{\partial Q_{N_r}(V,T)}{\partial T} + \sum_{N_r=0}^{\infty} \frac{N_r z^{N_r-1} Q_{N_r}(V,T)}{z^{N_r} Q_{N_r}(V,T)}\left(\frac{\partial z}{\partial T}\right)_{\mu,V} \tag{16}$$

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \sum_{N_r=0}^{\infty} \frac{1}{Q_{N_r}(V,T)} \frac{\partial Q_{N_r}(V,T)}{\partial T} + \sum_{N_r=0}^{\infty} N_r z^{-1}\left(\frac{\partial z}{\partial T}\right)_{\mu,V} \tag{17}$$

The first term in this sum is simply $\left(\frac{\partial q}{\partial T}\right)_{z,V}$, as found in equation (11). Make this substitution.

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \left(\frac{\partial q}{\partial T}\right)_{z,V} + \sum_{N_r=0}^{\infty} N_r z^{-1}\left(\frac{\partial z}{\partial T}\right)_{\mu,V} \tag{18}$$

Now, use equation (3.3.11) in the book to find $\left(\frac{\partial z}{\partial T}\right)_{\mu,V}$

$$z \equiv e^{\mu/kT} \tag{19}$$

$$\left(\frac{\partial z}{\partial T}\right)_{\mu,V} = e^{\mu/kT}\left(-\frac{\mu}{kT^2}\right) \tag{20}$$

$$\left(\frac{\partial z}{\partial T}\right)_{\mu,V} = -z\frac{\mu}{kT^2} \tag{21}$$

Substitute equation (21) into equation (18).

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \left(\frac{\partial q}{\partial T}\right)_{z,V} + \sum_{N_r=0}^{\infty} N_r z^{-1}\left(-z\frac{\mu}{kT^2}\right) \tag{22}$$

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \left(\frac{\partial q}{\partial T}\right)_{z,V} + \sum_{N_r=0}^{\infty} -N_r\frac{\mu}{kT^2} \tag{23}$$

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \left(\frac{\partial q}{\partial T}\right)_{z,V} - \frac{\mu}{kT^2}\sum_{N_r=0}^{\infty} N_r \tag{24}$$

The sum in the last term is summing N_r over all N. Therefore, this sum can be written as:

$$\sum_{N_r=0}^{\infty} N_r = N \tag{25}$$

Use this result in equation (24).

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \left(\frac{\partial q}{\partial T}\right)_{z,V} - \frac{N\mu}{kT^2} \tag{26}$$

$$\left(\frac{\partial q}{\partial T}\right)_{z,V} = \left(\frac{\partial q}{\partial T}\right)_{\mu,V} + \frac{N\mu}{kT^2} \tag{27}$$

Use the result of equation (27) in equation (5).

$$S = k\left[T\left(\left(\frac{\partial q}{\partial T}\right)_{\mu,V} + \frac{N\mu}{kT^2}\right) - \frac{N\mu}{kT} + q\right] \tag{28}$$

$$S = k\left[T\left(\frac{\partial q}{\partial T}\right)_{\mu,V} + \frac{N\mu}{kT} - \frac{N\mu}{kT} + q\right] \tag{29}$$

$$S = k\left[T\left(\frac{\partial q}{\partial T}\right)_{\mu,V} + q\right] \tag{30}$$

We can rewrite q in the following way:

$$q = q\left(\frac{\partial}{\partial T}T\right)_{\mu,V} \tag{31}$$

Substitute equation (31) into equation (30).

$$S = k\left[T\left(\frac{\partial q}{\partial T}\right)_{\mu,V} + q\left(\frac{\partial}{\partial T}T\right)_{\mu,V}\right] \tag{32}$$

It is clear from the form of equation (32) that the terms inside the bracket resemble the product rule of T and q differentiated with respect to temperature at constant μ and V. Rewrite equation (32) as such.

$$S = k\left[\frac{\partial}{\partial T}(Tq)_{\mu,V}\right] \tag{33}$$

$$\boxed{S = k\left[\frac{\partial}{\partial T}(Tq)\right]_{\mu,V}}$$

4.8 Determine the grand partition function of a gaseous system of "magnetic" atoms (with $J = 1/2$ and $g = 2$) that can have, in addition to the kinetic energy, a magnetic potential energy equal to $\mu_B H$ or $-\mu_B H$, depending on their orientation with respect to an applied magnetic field H. Derive an expression for the magnetization of the system, and calculate how much heat will be given off by the system when the magnetic field is reduced from H to zero at constant volume and constant temperature.

Equation (4.3.15) gives the grand partition function.

$$\mathfrak{Q} \equiv \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T) \tag{34}$$

Find the canonical partition function. From equation (3.5.5) in the book, we know the canonical partition function for a system of indistinguishable particles is given as:

$$Q_N(V,T) \equiv \frac{1}{N!h^{3N}} \int e^{-\beta H(q,p)} d\omega \tag{35}$$

For this problem, the Hamiltonian is:

$$H(p,q) = \sum_{i=1}^{N} \frac{p_i^2}{2m} \pm \mu_B H \tag{36}$$

Find the canonical partition function.

$$Q_N(V,T) = \frac{1}{N!h^{3N}} \int \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} \pm \mu_B H\right) d\omega \tag{37}$$

$$Q_N(V,T) = \frac{1}{N!h^{3N}} \int \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} \pm \mu_B H\right) \Pi_{i=1}^{N}\left(d^3q_i d^3p_i\right) \tag{38}$$

Following the example in the book, integration over the spatial coordinates yields a factor of V^N, following a product of N integrals. We can therefore rewrite equation (38) as:

$$Q_N(V,T) = \frac{V^N}{N!h^{3N}}\left[\int_0^\infty \exp\left(-\beta\frac{p^2}{2m} \mp \beta\mu_B H\right) 4\pi p^2 dp\right]^N \tag{39}$$

$$Q_N(V,T) = \frac{V^N}{N!h^{3N}}\left[\int_0^\infty e^{\mp\beta\mu_B H} \exp\left(-\beta\frac{p^2}{2m}\right) 4\pi p^2 dp\right]^N \tag{40}$$

$$Q_N(V,T) = \frac{V^N}{N!h^{3N}} 2\cosh\left(\mu_B H/kT\right)^N \left[\int_0^\infty \exp\left(-\beta\frac{p^2}{2m}\right) 4\pi p^2 dp\right]^N \tag{41}$$

$$Q_N(V,T) = \frac{1}{N!}\left(\frac{2V\cosh\left(\mu_B H/kT\right)}{h^3}\right)^N \left[\int_0^\infty \exp\left(-\beta\frac{p^2}{2m}\right) 4\pi p^2 dp\right]^N \tag{42}$$

$$Q_N(V,T) = \frac{1}{N!}\left(\frac{2V\cosh\left(\mu_B H/kT\right)}{h^3}\right)^N \left[\int_0^\infty \exp\left(-\frac{p^2}{2mkT}\right) 4\pi p^2 dp\right]^N \tag{43}$$

$$Q_N(V,T) = \frac{1}{N!}\left(\frac{8\pi V\cosh\left(\mu_B H/kT\right)}{h^3}\right)^N \left[\int_0^\infty \exp\left(-\frac{p^2}{2mkT}\right) p^2 dp\right]^N \tag{44}$$

Use the following Gaussian integral to reduce equation (44).

$$\int_0^\infty x^{2n} \exp\left(-x^2/a\right) dx = \sqrt{\pi}\frac{a^{2n+1}\left(2n-1\right)!!}{2^{n+1}} \tag{45}$$

$$n = 1 \tag{46}$$

$$a = \sqrt{2mkT} \tag{47}$$

Plugging in to equation (44) gives:

$$Q_N(V,T) = \frac{1}{N!}\left(\frac{8\pi V\cosh\left(\mu_B H/kT\right)}{h^3}\right)^N \left[\sqrt{\pi}\frac{\left(2mkT\right)^{3/2}\left(1\right)!!}{2^2}\right]^N \tag{48}$$

$$Q_N(V,T) = \frac{1}{N!}\left(\frac{8\pi V\cosh\left(\mu_B H/kT\right)}{h^3}\right)^N \left[\sqrt{\pi}\frac{\left(2mkT\right)^{3/2}}{4}\right]^N \tag{49}$$

$$Q_N(V,T) = \frac{1}{N!}\left(\frac{8\pi V\cosh\left(\mu_B H/kT\right)}{h^3}\frac{\sqrt{\pi}\left(2mkT\right)^{3/2}}{4}\right)^N \tag{50}$$

$$Q_N(V,T) = \frac{1}{N!}\left(\frac{2\pi^{3/2} V\cosh\left(\mu_B H/kT\right)}{h^3}\frac{\left(2mkT\right)^{3/2}}{1}\right)^N \tag{51}$$

$$Q_N(V,T) = \frac{1}{N!}\left(\frac{2V\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^N \tag{52}$$

Since 2 electrons can share a given state ($J = 1/2$, $g = 2$), multiply this partition function by 2.

$$Q_N(V,T) = \frac{2}{N!}\left(\frac{2V\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^N \tag{53}$$

Use this result in equation (34) to find the grand canonical partition function.

$$\mathfrak{Q} = \sum_{N_r=0}^\infty z^{N_r}\frac{2}{N_r!}\left(\frac{2V\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^{N_r} \tag{54}$$

$$\mathfrak{Q} = 2\sum_{N_r=0}^\infty \frac{1}{N_r!}\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^{N_r} \tag{55}$$

Equation (55) resembles the Taylor series for e^x.

$$\mathcal{Q} = 2\exp\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right) \tag{56}$$

$$\boxed{\mathcal{Q}\left(z,V,T\right) = 2\exp\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)}$$

Find the Helmholtz Free Energy, using equation (4.3.19) in the book.

$$A \equiv NkT\ln z - kT\ln\mathcal{Q}\left(z,V,T\right) \tag{57}$$

$$A = NkT\ln z - kT\ln\left(2\exp\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\right) \tag{58}$$

$$A = NkT\ln z - kT\ln\left(\exp\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\right)^2 \tag{59}$$

$$A = NkT\ln z - kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2 \tag{60}$$

Now, find the magnetization using equation (3.9.4) in the book.

$$M \equiv -\left(\frac{\partial A}{\partial H}\right)_T \tag{61}$$

$$M = -\frac{\partial}{\partial H}\left(NkT\ln z - kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2\right)_T \tag{62}$$

$$M = -\frac{\partial}{\partial H}\left(-kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2\right)_T \tag{63}$$

$$M = kT\frac{\partial}{\partial H}\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2 \tag{64}$$

$$M = 2kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\frac{\partial}{\partial H}\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)_T \tag{65}$$

$$M = 2kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\left(\frac{2Vz}{h^3}\left(2\pi mkT\right)^{3/2}\right)\frac{\partial}{\partial H}\left(\cosh\left(\mu_B H/kT\right)\right) \tag{66}$$

$$M = 2kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\left(\frac{2Vz}{h^3}\left(2\pi mkT\right)^{3/2}\right)\left(\sinh\left(\mu_B H/kT\right)\right)\left(\frac{\mu_B}{kT}\right) \tag{67}$$

$$M = 2\mu_B\left(\frac{2Vz}{h^3}\left(2\pi mkT\right)^{3/2}\right)\left(\frac{2Vz}{h^3}\left(2\pi mkT\right)^{3/2}\right)\cosh\left(\mu_B H/kT\right)\sinh\left(\mu_B H/kT\right) \tag{68}$$

$$M = 2\mu_B\left(\frac{2Vz}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2\cosh\left(\mu_B H/kT\right)\sinh\left(\mu_B H/kT\right) \tag{69}$$

$$M = 2\mu_B\left(\frac{2Vz}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2\cosh\left(\mu_B H/kT\right)\sinh\left(\mu_B H/kT\right) \tag{70}$$

Find $N(z,V,T)$, using equation (4.3.17) in the book, to simplify this result.

$$N(z,V,T) \equiv z\left[\frac{\partial}{\partial z}\ln \mathcal{Q}(z,V,T)\right] \tag{71}$$

$$N(z,V,T) = z\left[\frac{\partial}{\partial z}\ln\left(2\exp\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)\right)\right] \tag{72}$$

$$N(z,V,T) = z\left[\frac{\partial}{\partial z}\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)^2\right] \tag{73}$$

$$N(z,V,T) = z\left[2\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)\frac{\partial}{\partial z}\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)\right] \tag{74}$$

$$N(z,V,T) = z\left[2\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)\left(\frac{2V\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)\right] \tag{75}$$

$$N(z,V,T) = z\left[2z\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)^2\right] \tag{76}$$

$$N(z,V,T) = 2z^2\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)^2 \tag{77}$$

$$z^2 = \frac{N(z,V,T)}{2\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)^2} \tag{78}$$

Use this result in equation (70).

$$M = 2\mu_B z^2\left(\frac{2V}{h^3}(2\pi mkT)^{3/2}\right)^2\cosh(\mu_B H/kT)\sinh(\mu_B H/kT) \tag{79}$$

$$M = 2\mu_B\left(\frac{N(z,V,T)}{2\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)^2}\right)\left(\frac{2V}{h^3}(2\pi mkT)^{3/2}\right)^2\cosh(\mu_B H/kT)\sinh(\mu_B H/kT) \tag{80}$$

$$M = 2\mu_B\left(\frac{N(z,V,T)}{2}\right)\frac{\left(\frac{2V}{h^3}(2\pi mkT)^{3/2}\right)^2}{\left(\frac{2Vz}{h^3}(2\pi mkT)^{3/2}\right)^2}\frac{\cosh(\mu_B H/kT)}{(\cosh(\mu_B H/kT))^2}\sinh(\mu_B H/kT) \tag{81}$$

$$M = 2\mu_B\left(\frac{N(z,V,T)}{2}\right)\frac{1}{\cosh(\mu_B H/kT)}\sinh(\mu_B H/kT) \tag{82}$$

$$M = \mu_B N(z,V,T)\frac{\sinh(\mu_B H/kT)}{\cosh(\mu_B H/kT)} \tag{83}$$

$$M = N(z,V,T)\,\mu_B\tanh(\mu_B H/kT) \tag{84}$$

This is the same result as the magnetization of a paramagnet!

$$\boxed{M = N(z,V,T)\,\mu_B\tan(\mu_B H/kT)}$$

where

$$N(z,V,T) = 2z^2\left(\frac{2Vz\cosh(\mu_B H/kT)}{h^3}(2\pi mkT)^{3/2}\right)^2 \tag{85}$$

as found in equation (77) earlier.

Now, calculate the heat given off by the system when the magnetic field is reduced from H to 0 at constant volume and constant temperature. Start by deriving the entropy of the system, S, using equation (4.3.20) in the book.

$$S \equiv kT\left(\frac{\partial q}{\partial T}\right)_{z,V} - Nk\ln z + kq \tag{86}$$

$$S = kT\frac{\partial}{\partial T}\left(\ln 2\exp\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\right)_{z,V} \tag{87}$$

$$- Nk\ln z + k\ln 2\exp\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right) \tag{88}$$

$$S = kT\frac{\partial}{\partial T}\left(\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2\right)_{z,V} \tag{89}$$

$$- Nk\ln z + k\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2 \tag{90}$$

$$S = 2kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\frac{\partial}{\partial T}\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)_{z,V} \tag{91}$$

$$- Nk\ln z + k\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2 \tag{92}$$

$$S = 2kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\frac{3}{2}\left(2\pi mkT\right)^{1/2}\left(2\pi mk\right)\right. \tag{93}$$

$$\left.+\left(2\pi mkT\right)^{3/2}\frac{2Vz\sinh\left(\mu_B H/kT\right)}{h^3}\left(-\frac{\mu_B H}{kT^2}\right)\right) - Nk\ln z + k\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2 \tag{94}$$

Find the change in entropy, ΔS.

$$\Delta S = S_f - S_i \tag{95}$$

$$S_f = S\left(H = 0\right) \tag{96}$$

$$S_f = -Nk\ln z \tag{97}$$

$$S_i = 2kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\frac{3}{2}\left(2\pi mkT\right)^{1/2}\left(2\pi mk\right)\right. \tag{98}$$

$$\left.+\left(2\pi mkT\right)^{3/2}\frac{2Vz\sinh\left(\mu_B H/kT\right)}{h^3}\left(-\frac{\mu_B H}{kT^2}\right)\right) - Nk\ln z + k\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2 \tag{99}$$

$$\Delta S = -2kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\frac{3}{2}\left(2\pi mkT\right)^{1/2}\left(2\pi mk\right)\right. \tag{100}$$

$$\left.+\left(2\pi mkT\right)^{3/2}\frac{2Vz\sinh\left(\mu_B H/kT\right)}{h^3}\left(-\frac{\mu_B H}{kT^2}\right)\right) - k\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2 \tag{101}$$

Use the definition of heat to find the heat released by the system.

$$\Delta Q = T\Delta S \tag{102}$$

$$\Delta Q = -2kT^2\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\frac{3}{2}\left(2\pi mkT\right)^{1/2}\left(2\pi mk\right)\right. \tag{103}$$

$$\left.+\left(2\pi mkT\right)^{3/2}\frac{2Vz\sinh\left(\mu_B H/kT\right)}{h^3}\left(-\frac{\mu_B H}{kT^2}\right)\right) - kT\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2 \tag{104}$$

$$\Delta Q = -2kT^2\left(\frac{2V\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)\left(\frac{2Vz^2\cosh\left(\mu_B H/kT\right)}{h^3}\frac{3}{2}\left(2\pi mkT\right)^{1/2}\left(2\pi mk\right)\right. \tag{105}$$

$$\left.+\left(2\pi mkT\right)^{3/2}\frac{2Vz^2\sinh\left(\mu_B H/kT\right)}{h^3}\left(-\frac{\mu_B H}{kT^2}\right)\right) - kTz^2\left(\frac{2V\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2 \tag{106}$$

Make the substitution for z^2, as found in equation (78).

$$\Delta Q = -2kT^2 \left(\frac{2V\cosh\left(\mu_B H/kT\right)}{h^3} \left(2\pi mkT\right)^{3/2} \right) \left(\frac{2V \left(\frac{N(z,V,T)}{2\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2} \right) \cosh\left(\mu_B H/kT\right)}{h^3} \right. \tag{107}$$

$$\times \frac{3}{2}\left(2\pi mkT\right)^{1/2}\left(2\pi mk\right) \tag{108}$$

$$\left. + \left(2\pi mkT\right)^{3/2} \frac{2V \left(\frac{N(z,V,T)}{2\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2} \right) \sinh\left(\mu_B H/kT\right)}{h^3} \left(-\frac{\mu_B H}{kT^2} \right) \right) \tag{109}$$

$$- kT \left(\frac{N\left(z,V,T\right)}{2\left(\frac{2Vz\cosh\left(\mu_B H/kT\right)}{h^3}\left(2\pi mkT\right)^{3/2}\right)^2} \right) \left(\frac{2V\cosh\left(\mu_B H/kT\right)}{h^3} \left(2\pi mkT\right)^{3/2} \right)^2 \tag{110}$$

$$\Delta Q = -kT^2 \left(\left(2\pi mkT\right)^{3/2} \right) \left(\left(\frac{N\left(z,V,T\right)}{\left(z\left(2\pi mkT\right)^{3/2}\right)^2} \right) \frac{3}{2}\left(2\pi mkT\right)^{1/2}\left(2\pi mk\right) \right. \tag{111}$$

$$\left. + \left(2\pi mkT\right)^{3/2} \left(\frac{N\left(z,V,T\right)}{\left(z\left(2\pi mkT\right)^{3/2}\right)^2} \right) \tanh\left(\mu_B H/kT\right) \left(-\frac{\mu_B H}{kT^2} \right) \right) - kT \left(\frac{N\left(z,V,T\right)}{2\left(z\right)^2} \right) \tag{112}$$

$$\Delta Q = -kT^2 \left(\left(2\pi mkT\right)^{3/2} \right) \left(\left(\frac{N\left(z,V,T\right)}{\left(z\left(2\pi mkT\right)^{3/2}\right)^2} \right) \frac{3}{2}\frac{\left(2\pi mkT\right)^{3/2}}{T} \right. \tag{113}$$

$$\left. + \left(2\pi mkT\right)^{3/2} \left(\frac{N\left(z,V,T\right)}{\left(z\left(2\pi mkT\right)^{3/2}\right)^2} \right) \tanh\left(\mu_B H/kT\right) \left(-\frac{\mu_B H}{kT^2} \right) \right) - kT \left(\frac{N\left(z,V,T\right)}{2\left(z\right)^2} \right) \tag{114}$$

$$\Delta Q = -kT^2 \left(\left(\frac{N\left(z,V,T\right)}{\left(z\right)^2} \right) \frac{3}{2}\frac{1}{T} + \left(\frac{N\left(z,V,T\right)}{\left(z\right)^2} \right) \tanh\left(\mu_B H/kT\right) \left(-\frac{\mu_B H}{kT^2} \right) \right) - kT \left(\frac{N\left(z,V,T\right)}{2\left(z\right)^2} \right) \tag{115}$$

$$\Delta Q = -kT^2 \left(\frac{N\left(z,V,T\right)}{\left(z\right)^2} \right) \frac{3}{2T} - kT^2 \left(\frac{N\left(z,V,T\right)}{\left(z\right)^2} \right) \tanh\left(\mu_B H/kT\right) \left(-\frac{\mu_B H}{kT^2} \right) - kT \left(\frac{N\left(z,V,T\right)}{2\left(z\right)^2} \right) \tag{116}$$

$$\Delta Q = \frac{N\left(z,V,T\right)}{z^2} \left(-kT^2\frac{3}{2T} - kT^2\tanh\left(\mu_B H/kT\right) \left(-\frac{\mu_B H}{kT^2} \right) - kT\left(\frac{1}{2}\right) \right) \tag{117}$$

$$\Delta Q = \frac{N\left(z,V,T\right)}{z^2} \left(\frac{-3kT^2}{2T} + \tanh\left(\mu_B H/kT\right) \left(\frac{\mu_B H}{1} \right) - \frac{kT}{2} \right) \tag{118}$$

$$\Delta Q = \frac{N\left(z,V,T\right)}{z^2} \left(\frac{-3kT}{2} + \mu_B H\tanh\left(\mu_B H/kT\right) - \frac{kT}{2} \right) \tag{119}$$

$$\Delta Q = \frac{N\left(z,V,T\right)}{z^2} \left(\frac{-4kT}{2} + \mu_B H\tanh\left(\frac{\mu_B H}{kT}\right) \right) \tag{120}$$

$$\Delta Q = \frac{N\left(z,V,T\right)}{z^2} \left(\mu_B H\tanh\left(\frac{\mu_B H}{kT}\right) - 2kT \right) \tag{121}$$

$$\boxed{\Delta Q = \frac{N\left(z,V,T\right)}{z^2} \left(\mu_B H\tanh\left(\frac{\mu_B H}{kT}\right) - 2kT \right)}$$

where

$$N\left(z,V,T\right)=2z^{2}\left(\frac{2Vz\cosh\left(\mu_{B}H/kT\right)}{h^{3}}\left(2\pi mkT\right)^{3/2}\right)^{2} \tag{122}$$