Equilibrium in a Magnetic Gas

A gas of atoms with spin $\frac{1}{2}$ and magnetic moment μ has volume V and is in a magnetic field B.

The partition function for N atoms in equilibrium at temperature $T = 1/\beta$ is

$$Z(T,N) = \frac{1}{N!}\left[\frac{V}{\lambda_T^3}\left(e^{+\beta\mu B} + e^{-\beta\mu B}\right)\right]^N,$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mT}$.

A. Determine the Helmholtz free energy F in the thermodynamic limit.
(Stirling's approximation is $\log N! = N\log N - N$.)

$$F = -\frac{1}{\beta}\log Z = -T\left[N\log\frac{V}{\lambda_T^3} + \log\left(e^{+\beta\mu B} + e^{-\beta\mu B}\right) - \log(N!)\right]$$

$$\simeq -NT\left[\log\frac{V}{\lambda_T^3} + \log\left(e^{+\beta\mu B} + e^{-\beta\mu B}\right) - \log N + 1\right]$$

If the gas consists of N_+ atoms with spin up ($\uparrow$) and N_- atoms with spin down ($\downarrow$), the partition function is

$$Z(T,N_+,N_-) = \frac{1}{N_+!}\left[\frac{V}{\lambda_T^3}e^{-\beta\mu B}\right]^{N_+} \times \frac{1}{N_-!}\left[\frac{V}{\lambda_T^3}e^{+\beta\mu B}\right]^{N_-},$$

B. Explain the factors of $1/N_+!$ and $1/N_-!$.

The spin-up atoms are identical particles
and the spin-down atoms are distinct identical particles.

The Helmholtz free energy $F_+ + F_-$ is the sum of terms from $\uparrow$ and $\downarrow$ atoms.

C. Determine F_+ in the thermodynamic limit.

$$F_+ = -N_+T\left[\log\frac{V}{\lambda_T^3} + \log\left(e^{-\beta\mu B}\right) - \log N_+ + 1\right]$$

$$= -N_+T\left[\log\frac{V}{\lambda_T^3} - \beta\mu B - \log N_+ + 1\right]$$

The thermodynamic relation for the Helmholtz free energy is

$$d(F_+ + F_-) = -S\,dT - P\,dV + \mu_+\,dN_+ + \mu_-\,dN_-.$$

D. Determine the chemical potential μ_+.

$$\mu_+ = \left(\frac{\partial(F_+ + F_-)}{\partial N_+}\right)_{T,V,N_-} = \left(\frac{\partial F_+}{\partial N_+}\right)_{T,V} = -T\left[\log\frac{V}{\lambda_T^3} - \beta\mu B - \log N_+ + 1\right] - N_+T\left[-\frac{1}{N_+}\right]$$

$$= -T\left[\log\frac{V}{\lambda_T^3} - \log N_+ - \beta\mu B\right]$$

The spin of an atom can be flipped by a collision with another atom.
The net effect is the reaction $\uparrow \ \longleftrightarrow \ \downarrow$.
The condition for chemical equilibrium from this reaction is $\mu_+ = \mu_-$.
E. Simplify this condition by eliminating its dependence on the volume V.

$$-T\left[\log \frac{V}{\lambda_T^3} - \log N_+ - \beta\mu B\right] = -T\left[\log \frac{V}{\lambda_T^3} - \log N_- + \beta\mu B\right]$$

$$\log N_+ + \beta\mu B = \log N_- - \beta\mu B$$

Consider the case where the total number of atoms is N.
F. Express the chemical equilibrium condition as an equation that can be solved for N_+ as a function of N and $\beta\mu B$.
(The solution is $N_+ = \frac{1}{e^{2\beta\mu B}+1} N$.)

$$\log N_+ + \beta\mu B = \log (N - N_+) - \beta\mu B$$

If a system that is not in equilibrium is held at constant temperature, its Helmholtz free energy will decrease. When it reaches equilibrium, the Helmholtz free energy will have its minimum possible value.
G. Express $F_+ + F_-$ as a function of N and N_+.

$$F_+ + F_- = -N_+ T\left[\log \frac{V}{\lambda_T^3} - \log N_+ - \beta\mu B + 1\right]$$
$$-(N-N_+) T\left[\log \frac{V}{\lambda_T^3} - \log (N-N_+) + \beta\mu B + 1\right]$$

H. Express the minimization condition for the Helmholtz free energy as the vanishing of a derivative of $F_+ + F_-$.

$$\left(\frac{\partial}{\partial N_+}(F_+ + F_-)\right)_{T,V,N} = 0$$

I. Without calculating the derivative explicitly, show that this minimization condition coincides with the condition for chemical equilibrium.

$$\frac{\partial F_+}{\partial N_+} + \frac{\partial F_-}{\partial N_-} \frac{d(N-N_+)}{d N_+} = 0$$

$$\mu_+ + \mu_- (-1) = 0$$

If you insert the solution N_+ to the equilibrium condition into $F_+ + F_-$, it reduces (after some complicated algebra) to the Helmholtz free energy F from part A.