

In this solution, unit system $h = 1 = k_B$ is used. One can restore it by dimensional analysis $\beta = \frac{1}{T}$

3.1 Vertical column of ideal gas

Canonical energy per particle is given by $\epsilon = T + U = \frac{p^2}{2m} + mgh$. We integrate through phase space for partition function Z_{1p} since energy is continuous.

$$\begin{aligned}
 Z_{1p} &= \int dV \int d^3\vec{p} e^{-\beta\epsilon} \\
 &= \int dS dh \int d^3\vec{p} e^{-\beta\left[\frac{p^2}{2m} + mgh\right]} \\
 &= S \int_0^{h_0} dh e^{-\beta mgh} \prod_{i=1}^3 \int_{-\infty}^{\infty} dp_i e^{-\beta \frac{p_i^2}{2m}} \\
 &= S \frac{1}{\beta mg} [1 - e^{-\beta mgh_0}] \left(\frac{2\pi m}{\beta}\right)^{3/2} \equiv \frac{ST}{mg} [1 - e^{-mgh_0/T}] \left(\frac{2\pi mT}{h^2}\right)^{3/2}
 \end{aligned} \tag{1}$$

After obtaining partition function Z_{1p} , $Z = \frac{Z_{1p}^N}{N!}$, it's easy for us to find free energy F and internal energy E

$$\begin{aligned}
 F &= -\frac{1}{\beta} \log(Z) = -\frac{3N}{2\beta} \log \frac{2\pi m}{\beta} - \frac{N}{\beta} \log \frac{S(1 - e^{-\beta mgh_0})}{N\beta mg} - \frac{N}{\beta} \\
 E &= -\frac{\partial}{\partial \beta} \log(Z) = -N \frac{\partial}{\partial \beta} \log(Z_{1p}) = \frac{3N}{2} \frac{\partial}{\partial \beta} \log \beta + N \frac{\partial}{\partial \beta} [\log \beta - \log(1 - e^{-\beta mgh_0})] \\
 &= \frac{5N}{2\beta} - \frac{Nmgh_0 e^{-\beta mgh_0}}{1 - e^{-\beta mgh_0}} = \frac{5N}{2\beta} - \frac{Nmgh_0}{e^{\beta mgh_0} - 1} \\
 h_{c.m.} &= \frac{\int Nmhe^{-\beta\epsilon}}{\int Nme^{-\beta\epsilon}} = -\frac{1}{\beta m} \frac{\partial}{\partial g} \log Z_{1p} = \frac{1}{\beta mg} - \frac{h_0}{e^{\beta mgh_0} - 1} \\
 C &= \frac{\partial E}{\partial T} = \frac{5N}{2} - N e^{\beta mgh_0} \left[\frac{\beta mgh_0}{e^{\beta mgh_0} - 1} \right]^2
 \end{aligned} \tag{2}$$

Consider two cases. First $mgh_0 \gg T \Rightarrow \beta mgh_0 \gg 1 \Rightarrow e^{-\beta mgh_0} \ll 1$

$$h_{c.m.} = \frac{1}{\beta mg} ; C = \frac{5N}{2} \tag{3}$$

In another case $mgh_0 \ll T \Rightarrow \beta mgh_0 \ll 1 \Rightarrow e^{-\beta mgh_0} \simeq 1 - \beta mgh_0 + \frac{(\beta mgh_0)^2}{2}$

$$\begin{aligned}
 h_{c.m.} &\simeq \frac{1}{\beta mg} - \frac{h_0}{\beta mgh_0 + \frac{1}{2}(\beta mgh_0)^2} \simeq \frac{h_0}{2} \\
 C &\simeq \frac{5N}{2} - N \left[\frac{\beta mgh_0}{\beta mgh_0} \right]^2 = \frac{3N}{2}
 \end{aligned} \tag{4}$$

3.2 Ultrarelativistic gas

Ultrarelativistic gas has $\epsilon = c|\vec{p}|$. It's continuous spectrum thus we need to integrate through phase space for a single particle. $v = \frac{V}{N}$

$$\begin{aligned}
Z_{1p} &= \int dV \int d^3\vec{p} e^{-\beta\epsilon} = 4\pi V \int_0^\infty p^2 e^{-\beta cp} dp = 4\pi V \frac{2}{(\beta c)^3} \Rightarrow Z = \frac{Z_{1p}^N}{N!} \\
F &= \frac{-1}{\beta} \log Z = \frac{-N}{\beta} [\log(8\pi v) - 3 \log(\beta c) + 1] \\
E &= -\frac{\partial}{\partial \beta} \log Z = \frac{3N}{\beta} \\
S &= \frac{E - F}{T} = \beta(E - F) = N[4 - 3 \log(\beta c) + \log(8\pi v)] \\
p &= -\left(\frac{\partial F}{\partial V}\right)_\beta = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z = \frac{1}{\beta} \frac{\partial}{\partial v} \log Z_{1p} = \frac{1}{\beta v}
\end{aligned} \tag{5}$$

In an adiabatic expansion $dQ = 0 \Rightarrow dE = -pdv$. Express p , T in function of v

$$\begin{aligned}
3dT &= dE = -pdv = -\frac{Tdv}{v} \Rightarrow Tv^{\frac{1}{3}} = const \\
T &= pv \Rightarrow pv^{\frac{4}{3}} = const
\end{aligned} \tag{6}$$

3.3 Dipole molecules

For diatomic particle with permanent electric dipole moment \vec{b} the total energy can be expressed as $\epsilon = \epsilon_{c.m.} + \epsilon_{rot} + \epsilon_{ang} = \frac{\vec{p}^2}{2m} + \frac{1}{2} \mathbb{I}_{ij} \omega_i \omega_j - \vec{b} \cdot \vec{\mathcal{E}}$. We can separate center of mass frame and rotation frame contribution $Z_{1p}(T, \vec{\mathcal{E}}) = Z_{c.m.}(T) Z_{rot}(T) Z_{ang}(T, \vec{\mathcal{E}})$. We are only interested in Z_{ang} in this case. Assume $\vec{\mathcal{E}} = \mathcal{E} \hat{z}$

$$Z_{ang} = \int d\Omega e^{\beta \vec{b} \cdot \vec{\mathcal{E}}} = 2\pi \int_{-\pi}^{\pi} \sin \theta d\theta e^{\beta b \mathcal{E} \cos \theta} = 2\pi \frac{2 \sinh(\beta b \mathcal{E})}{\beta b \mathcal{E}} \tag{7}$$

Calculate angular probability distribution by

$$w = \frac{e^{-\beta b \mathcal{E} \cos \theta}}{Z_{ang}} \Rightarrow \frac{\partial w}{\partial \theta} = \frac{2\pi \beta b \mathcal{E} \sin \theta e^{\beta b \mathcal{E} \cos \theta}}{Z_{ang}} = \frac{(\beta b \mathcal{E})^2 \sin \theta e^{\beta b \mathcal{E} \cos \theta}}{2 \sinh \beta b \mathcal{E}} \tag{8}$$

(No points will be subtracted if 2π is not present. $\beta b \mathcal{E}$ will have power 1 after normalization.)

There are two ways to find polarization: one by definition, the other via energy

$$\begin{aligned}
1. P(T, \mathcal{E}) &= \frac{\sum_{\text{dipole}} \int d\Omega b \cos \theta e^{-\beta \epsilon_{ang}}}{\int d\Omega e^{-\beta \epsilon_{ang}}} = \frac{N}{\beta} \frac{\partial}{\partial \mathcal{E}} \log Z_{ang} = Nb \coth(\beta b \mathcal{E}) - \frac{N}{\beta \mathcal{E}} \\
2. P(T, \mathcal{E}) &= -\frac{E}{\mathcal{E}} = \frac{1}{\mathcal{E}} \frac{\partial}{\partial \beta} \log Z_{ang}^N = \frac{N}{\mathcal{E}} \left[b \mathcal{E} \coth(\beta b \mathcal{E}) - \frac{1}{\beta} \right]
\end{aligned} \tag{9}$$

In limit $T \rightarrow \infty, \Rightarrow \beta \rightarrow 0$

$$P(\beta \rightarrow 0, \mathcal{E}) = \lim_{\beta \rightarrow 0} Nb \frac{1 + \frac{(\beta b \mathcal{E})^2}{2}}{\beta b \mathcal{E}} - \frac{N}{\beta \mathcal{E}} = 0 \tag{10}$$

As we know in high temperature, thermal fluctuation causes dipoles pointing in random direction, leaving material unpolarized. We may also check in $T \rightarrow 0, \beta \rightarrow \infty$ limit, $P(\beta \rightarrow \infty, \mathcal{E}) = Nb$. This also matches our expectation. (Maximally polarized)

3.4 Paramagnetic medium II

N non-interacting magnetic dipoles. $\mu_z = \frac{m}{J}\mu$, where $-J \leq m \leq J$. Energy in an external magnetic field $\epsilon = -\frac{m}{J}\mu\mathcal{H}$.

(a)

Partition function

$$Z_N(T, \mathcal{H}) = \sum_{\text{state}} e^{-\beta\epsilon} = \frac{1}{N!} \left[\sum_{m=-J}^J e^{\beta \frac{m}{J} \mu \mathcal{H}} \right]^N = \frac{1}{N!} \left[\frac{e^{-\beta \mu \mathcal{H}} (1 - e^{\beta \frac{2J+1}{J} \mu \mathcal{H}})}{1 - e^{\beta \frac{1}{J} \mu \mathcal{H}}} \right]^N = \frac{1}{N!} \left[\frac{\sinh \beta \frac{2J+1}{2J} \mu \mathcal{H}}{\sinh \beta \frac{1}{2J} \mu \mathcal{H}} \right]^N \quad (11)$$

As $J = \frac{1}{2}$ (two level spin), we get the same result as HW 2.4.

(b)

$$\begin{aligned} F &= -\frac{1}{\beta} \log Z = N \left[\log N - 1 - \log \sinh \beta \frac{2J+1}{2J} \mu \mathcal{H} + \log \sinh \beta \frac{1}{2J} \mu \mathcal{H} \right] \\ E &= -\frac{\partial}{\partial \beta} \log Z = -N \mu \mathcal{H} \left[\frac{2J+1}{2J} \coth \beta \frac{2J+1}{2J} \mu \mathcal{H} - \frac{1}{2J} \coth \beta \frac{1}{2J} \mu \mathcal{H} \right] \\ M &= -\frac{E}{\mathcal{H}} = N \mu \left[\frac{2J+1}{2J} \coth \beta \frac{2J+1}{2J} \mu \mathcal{H} - \frac{1}{2J} \coth \beta \frac{1}{2J} \mu \mathcal{H} \right] \\ \chi_T &= \left(\frac{\partial M}{\partial \mathcal{H}} \right)_T = \frac{N \beta \mu^2}{4J^2} \left[\frac{1}{\sinh^2 \beta \frac{1}{2J} \mu \mathcal{H}} - \frac{(2J+1)^2}{\sinh^2 \beta \frac{2J+1}{2J} \mu \mathcal{H}} \right] \\ \left(\frac{\partial M}{\partial T} \right)_{\mathcal{H}} &= -\frac{N \mu^2 \mathcal{H} \beta^2}{4J^2} \left[\frac{1}{\sinh^2 \beta \frac{1}{2J} \mu \mathcal{H}} - \frac{(2J+1)^2}{\sinh^2 \beta \frac{2J+1}{2J} \mu \mathcal{H}} \right] \end{aligned} \quad (12)$$

(c)

$$C_{\mathcal{H}} = \left(\frac{\partial E}{\partial T} \right)_{\mathcal{H}} = \frac{d\beta}{dT} \left(\frac{\partial E}{\partial \beta} \right)_{\mathcal{H}} = \frac{\beta^2 N \mu^2 \mathcal{H}^2}{4J^2} \left[\frac{(2J+1)^2}{\sinh^2 \beta \frac{2J+1}{2J} \mu \mathcal{H}} - \frac{1}{\sinh^2 \beta \frac{1}{2J} \mu \mathcal{H}} \right] \quad (13)$$