Solutions

Chem 545  Problem Set #3  Spring

1) Consider $N$ independent and distinguishable particles with 4 states as shown:

\[ E_4 = 10 \epsilon \]

\[ E_2 = E_3 = \epsilon \]

\[ E_1 = 0 \]

Determine the partition function and appropriate relationships to enable you to make a reasonable sketch of $N_1/N$, $N_2/N$, $N_3/N$, $N_4/N$, $\bar{E}$, $S$, and $C_v$ vs. $T$ in units of $\theta = \epsilon/k$

2) MCQ 2-5

3) MCQ 2-13

4) MCQ 2-17

5) A gas composed of $N$ distinguishable particles in an ideal gas at a volume $V$ at a temperature $T$. The number of single-particle energy states in the range $E$ to $E+\Delta E$ is $4\pi V P^2 dP/h^3$. Find the partition function and the internal energy of the gas. Also, determine the specific heat. Note: in relativistic mechanics, the energy of a free particle is $H = c \sqrt{m^2c^2+p^2}$; therefore for a particle of extremely large energy, $E \approx pc$. (in text: external relativistic)
1) \[ \frac{N_1}{N} = \frac{e^{\theta}}{q} = \frac{1}{1 + 2e^{-\theta/T} + e^{-10\theta/T}} \]

\[ \frac{N_2}{N} = \frac{N_3}{N} = 2e^{-\theta/T} \]

\[ \frac{N_4}{N} = e^{-10\theta/T} \]

\[ \ln q = N \ln \left[ 1 + 2e^{-\theta/T} + e^{-10\theta/T} \right] \]

\[ S = k \ln q + \frac{E}{T} \]

\[ E = kT^2 \left( \frac{\partial \ln q}{\partial T} \right)_V \]

\[ C_V = \left( \frac{\partial E}{\partial T} \right)_V / N \]

\[ \left( \frac{\partial \ln q}{\partial T} \right)_V = N \left( 2 \frac{\theta^2}{T^2} e^{-\theta/T} + 10 \frac{\theta^2}{T^2} e^{-10\theta/T} \right) \]

\[ E = \frac{2Nk\theta \left[ e^{-\theta/T} + 5e^{-10\theta/T} \right]}{1 + 2e^{-\theta/T} + e^{-10\theta/T}} \]
We can derive this expression for $S$ by comparing the expression for $d\bar{E}$ derived from stat mech. with that for $d\bar{E}$ from thermodynamics (T.D.)

The mean energy is the ensemble average:

$$\bar{E} = \sum_j P_j \bar{E}_j$$  \((cf. \text{ McD (2-5)}\)\)

$$d\bar{E} = \sum_j dP_j \bar{E}_j + \sum_j P_j d\bar{E}_j$$

$$= \sum_j \bar{E}_j dP_j - \sum_j P_j \left(\frac{\partial \bar{E}_j}{\partial V}\right)$$

Since $P_j = \left(\frac{\partial E_j}{\partial V}\right)_N$ is the pressure of the $j$th state

$$= \sum_j E_j dP_j - P dV \quad (1)$$

Now, in the canonical ensemble,

$$P_j = \frac{e^{-\beta E_j}}{\Omega}$$

so

$$E_j = -kT \ln P_j - kT \ln \Omega$$

Substitute this into (1), hence

$$d\bar{E}_j = -kT \sum (\ln P_j + \ln \Omega) dP_j - P dV$$

$$= -kT \sum_j \ln P_j dP_j - P dV$$
this last step follows because
\[
\sum_{j} \ln d_{j} \, dP_{j} = \ln d \sum_{j} dP_{j} = \ln d \, d \left( \sum_{j} P_{j} \right) = \ln d \, d \left( \sum_{j} P_{j} \right) = 0.
\]

Next, we write
\[
d\bar{E} = -RT \, d \left( \sum_{j} P_{j} \ln P_{j} \right) - \bar{p} \, dV = T \, d \left( -P \sum_{j} P_{j} \ln P_{j} \right) - \bar{p} \, dV \tag{2} \]

From thermodynamics
\[
dE = T \, dS - \bar{p} \, dV \tag{3} \]

Invoking the ensemble postulate of Gibbs and comparing terms in opus (2) and (3), we find

\[
S = -k \sum_{j} P_{j} \ln P_{j}.
\]
For a particle in a cubic box of side $a$, the $n$th state has energy \((\text{McQ, p81})\)

\[
E_n = \frac{h^2 n^2}{8ma^2} \quad n^2 = n_x^2 + n_y^2 + n_z^2 \quad \text{and} \quad n_x, n_y, n_z = 0, 1, 2, 3, \ldots
\]

\[
= \frac{h^2 n^2}{8m} \, \sqrt{\frac{2}{3}} \quad \text{since} \quad V = a^3.
\]

and the corresponding pressure is

\[
P_n = -\left(\frac{\partial E_n}{\partial V}\right)_n
\]

\[
= \frac{\hbar^2 n^2}{8m} \, \sqrt{\frac{2}{3}} \, V^{-5/2}
\]

\[
= \frac{\hbar^2}{3} \, \frac{E_n}{V}
\]

(1)

Let's now average both sides of this eqn. in the canonical ensemble. The probability that state $n$ is occupied is

\[
P_n = \frac{e^{-\beta E_n}}{\Omega}
\]

(2)

thus

\[
\bar{P} = \sum_n P_n P_n
\]

\[
= \frac{1}{\Omega} \sum_n \frac{2}{3} \, \frac{E_n}{V} \, e^{-\beta E_n}
\]

using (1) and (3)
\[ P = \frac{3}{3} \cdot \frac{1}{V} \cdot \frac{1}{Q} \sum_n E_n e^{-\beta E_n} \]

\[ = \frac{a}{3} \frac{E}{V} \]

Further, \[ \bar{E} = \frac{3}{2} N k T \]

and so \[ \bar{P} V = N k T \]

the ideal gas eqn. or state!
An approximate partition function for a dense gas is

\[ Q = \frac{1}{N!} \left( \frac{2\pi m k T}{\hbar^2} \right)^{\frac{3N}{2}} (V - Nb)^N e^{\frac{aN^2}{VT}} \]

We want to find the corresponding eqn. of state so let's calculate the pressure. \{McQ eqn (2-22)\}

\[ P = kT \left( \frac{\partial}{\partial V} \ln Q \right)_{N,T} \]

Now

\[ \ln Q = -\ln N! + \frac{3N}{2} \ln \left( \frac{2\pi m k T}{\hbar^2} \right) + N \ln(V - Nb) + \frac{aN^2}{VT} \]  

So

\[ P = kT \left\{ \left( \frac{N}{V - Nb} \right) - \frac{aN^2}{VT} \right\} \]

\[ P(V - Nb) = NkT - \frac{aN^2}{V^2}(V - Nb) \]

We thus arrive at the eqn. of state of a \textit{van der Waals gas}:

\[ (P - \frac{aN^2}{V^2})(V - Nb) = NkT \]
\[ Q(v, T, N) := \left\{ \frac{v}{h^3} \int_{-\infty}^{+\infty} e^{-e/kT} \, dp_x \, dp_y \, dp_z \right\}^N \]

\[ e = c_p \]

\[ \iiint e^{-e/kT} \, dp_x \, dp_y \, dp_z = 4\pi \int_0^{\infty} e^{-e/kT} \rho^2 \, dp \]

\[ = 8\pi \left( \frac{kT}{c} \right)^3 \]

Using Stirling's Approx. and \( A = -kT \ln Q \)

\[ A = -NkT \ln \left( \frac{2\pi e^{k^3} v}{h^3 c^3} \right) \]

\[ P = -\left( \frac{\partial A}{\partial V} \right)_{T, N} = NkT \frac{\partial \ln V}{\partial V} = \frac{NkT}{V} \quad PV = NkT \]

\[ E = -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{A}{T} \right) \right]_{V, N} = T^2 Nk \, \frac{\partial (\ln T^3)}{\partial T} \]

\[ = 3NkT \]

\[ H = E + PV = 4NkT \]

\[ C_v = \left( \frac{\partial E}{\partial T} \right)_{v, N} = 3Nk \]

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_{p, N} = 4Nk \]