Physics 603 First Exam Solutions

1. Assume the gas is dilute, so $NV_0 \ll V$. A hard sphere of radius ρ excludes a volume of radius 2ρ, where $V_0 = \frac{4}{3}\pi(2\rho)^3$.

$\Omega \propto \prod_{j=0}^{N-1} (V - jV_0)$. $S = k \ln \Omega$. $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = k\left(\frac{\partial}{\partial V}\ln \Omega\right)_{E,N}$, where any multiplicative constant in Ω drops out.

$$\left(\frac{\partial}{\partial V}\ln\Omega\right)_{E,N} = \sum_{j=0}^{N-1}\frac{1}{V-jV_0} \approx \frac{1}{V}\sum_{j=0}^{N-1}\frac{1}{1-\frac{jV_0}{V}} \approx \frac{1}{V}\sum_{j=0}^{N-1}\left(1+\frac{jV_0}{V}\right)$$

$$\approx \frac{1}{V}\left(N + \frac{N^2}{2}\frac{V_0}{V}\right) \approx \frac{N}{V\left(1-\frac{N}{2}\frac{V_0}{V}\right)} = \frac{N}{V-\frac{NV_0}{2}}.$$ Then $p = \dfrac{NkT}{V - \frac{N}{2}V_0}$.

$\frac{N}{2}V_0 = \frac{1}{2}$ (total volume of hard spheres).

[Note: this evaluation of the sum amounts to a trapezoidal approximation, which is OK for $V_0 \ll 2NV$, which is weaker than we assumed. Probably better to just do the sum with the trapezoidal approximation.]

2. (a) S is not extensive because $N \ln V \to \lambda \ln \lambda$ when N and V scale with λ.

(b) Gibbs divided Ω by $N!$, so $\Delta \ln \Omega = -(N\ln N - N)$ and the $N \ln V$ is balanced by $-N\ln N$ to give $N \ln \frac{V}{N}$ which scales as λ.

(c) $$\Delta S_{\substack{\text{mixing}\\ \text{different}\\ \text{species}}} = N_1 k\left\{\ln\frac{V}{N_1} + \frac{5}{2} + \frac{3}{2}\ln\frac{2\pi m_1 kT_f}{h^2}\right\} +$$

$$+ N_2 k\left\{\frac{V}{N_2} + \frac{5}{2} + \frac{3}{2}\ln\frac{2\pi m_2 kT_f}{h^2}\right\} - N_1 k\left\{\ln\frac{V_1}{N_1} + \frac{5}{2} + \frac{3}{2}\ln\frac{2\pi m_1 kT_1}{h^2}\right\}$$

$$- N_2 k\left\{\frac{V_2}{N_2} + \frac{5}{2} + \frac{3}{2}\ln\frac{2\pi m_2 kT_2}{h^2}\right\} = N_1 k\left\{\ln\frac{V}{V_1} + \frac{3}{2}\ln\frac{T_f}{T_1}\right\}$$

$$+ N_2 k\left\{\ln\frac{V}{V_2} + \frac{3}{2}\ln\frac{T_f}{T_2}\right\}.$$

(d) If the temperatures were all the same $T_1 = T_2 = T_f$ then $\ln\frac{T_f}{T_1} = 0$, So the temperature mixing contribution is $\left(T_f = \frac{N_1 T_1 + N_2 T_2}{N_1 + N_2} \right)$

$\sum_{i=1}^{2} \frac{3}{2} N_i k \ln \frac{T_f}{T_i}$. To see the contribution from mixing of concentration assume the initial contributions are equal $n_1 = n_2 \equiv n$, or $\frac{N_1}{V_1} = \frac{N_2}{V_2} = n$
Then $\frac{N_1 + N_2}{V_1 + V_2} = \frac{V_1 n + V_2 n}{V_1 + V_2} = n$, so n is the final concentration ignoring the difference of species. $n = \frac{N_1 + N_2}{V_1 + V_2} = \frac{N_1 + N_2}{V}$. Then

$$\ln \frac{V}{V_1} = \ln \left(\frac{N_1 + N_2}{n} \frac{1}{V_1} \right) = \ln \left(\frac{N_1 + N_2}{n} \frac{n_1}{N_1} \right), \text{ since } N_1 = n_1 V_1.$$

Then get $\ln \left(\frac{n_i}{n} \right) + \ln \left(\frac{N_1 + N_2}{N_i} \right)$. If the concentrations are all the same, then $\ln \frac{n_i}{n} = 0$, so

$\sum_{i=1}^{2} N_i k \ln \frac{n_i}{n}$ is from concentration mixing. If the temperatures and concentrations are the same, the remaining term

$\sum_{i=1}^{2} N_i k \ln \frac{N_1 + N_2}{N_i}$ must come from species mixing. (mass alone does not label species, an excited state of a same mass counts as a different species.)

3. $\mathcal{Q} = \sum_{N_r, s} e^{-\alpha N_r - \beta E_s}$. Assume the adsorbed molecules have a one-dimensional spectrum. Then $N_r = 0$ or 1; $E_s = (s + \frac{1}{2}) \hbar\omega$, so at each site $\mathcal{Q}(z, 1, T) = 1 + e^{-\alpha} \sum_{s=0}^{\infty} e^{-\beta (s + \frac{1}{2}) \hbar\omega} = 1 + \frac{z}{2 \sinh \beta \frac{\hbar\omega}{2}}$

since $z = e^{-\alpha} = e^{\beta\mu}$. The sites are distinguishable, so

$$\mathcal{Q}(z, N_0, T) = \left[\mathcal{Q}(z, 1, T) \right]^{N_0}$$

$$N = \bar{N} = z \frac{\partial}{\partial z} \ln \mathcal{Q}(z, N_0, T) = N_0 z \frac{\partial}{\partial z} \ln \left(1 + \frac{z}{2 \sinh \left(\frac{\beta \hbar\omega}{2} \right)} \right)$$

$$= \frac{N_0 z}{2 \sinh \beta \frac{\hbar\omega}{2}} \frac{1}{1 + \frac{z}{2 \sinh \beta \frac{\hbar\omega}{2}}} = \frac{N_0 z}{z + 2 \sinh \beta \frac{\hbar\omega}{2}}. \quad z = \frac{\left(2 \sinh \left(\frac{\beta \hbar\omega}{2} \right) \right) N}{N_0 - N}$$

$$\mu = kT \ln z = kT \ln \frac{\left(2 \sinh \frac{\hbar\omega}{2kT} \right) N}{N_0 - N}$$

4. $Q_N = \sum_s e^{-\beta E_s}$, $\quad E = \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N = \dfrac{\sum_s E_s e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial E}{\partial \beta}\right)_V \frac{\partial \beta}{\partial T} = \left[\frac{-\sum_s E_s^2 e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} - \frac{\left(\sum_s E_s e^{-\beta E_s}\right)\left(\sum_s (-E_s) e^{-\beta E_s}\right)}{\left(\sum_s e^{-\beta E_s}\right)^2} \right]$$

$$\cdot \left(-\frac{1}{kT^2}\right) = \frac{1}{kT^2}\left[\langle E^2 \rangle - \langle E \rangle^2 \right] = \frac{1}{kT^2} \langle (\Delta E)^2 \rangle,$$ since

$$\langle (\Delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - 2\langle E \rangle \langle E \rangle + \langle E \rangle^2 = \langle E^2 \rangle - \langle E \rangle^2,$$

so

$$\langle (\Delta E)^2 \rangle = k T^2 C_V .$$