MPS PRACTICE PROBLEMS 2

SOLUTIONS

1 (a) $E = \frac{3}{2} N k_B T$

$$\Rightarrow \quad T = \frac{2}{3} \frac{E}{N k_B}$$

Then

$$S = N k_B \left(\frac{3}{2} \ln T + \ln V + \kappa \right)$$

$$= N k_B \left(\frac{3}{2} \ln \left(\frac{2}{3} \frac{E}{N k_B} \right) + \ln V + \kappa \right)$$

$$= N k_B \left(\frac{3}{2} \ln E - \frac{3}{2} \ln N + \ln V + \ln \left(\frac{2}{3 k_B} \right) + \kappa \right)$$

$$= N k_B \left(\frac{3}{2} \ln E - \frac{3}{2} \ln N + \ln V + \tilde{\kappa} \right)$$

where $\tilde{\kappa} = \ln \left(\frac{2}{3 k_B} \right) + \kappa$.

(b) In (a), we have $S(E, V, N)$, the entropy is expressed in terms of its "natural" variables. There are three equations of state that result from partial derivatives of S with respect to its natural variables. They are

- $$\frac{1}{T} = \frac{\partial S(E,V,N)}{\partial E}$$

$$= N k_B \cdot \frac{3}{2} \cdot \frac{1}{E}$$

$$\Rightarrow \boxed{E = \frac{3}{2} N k_B T}$$

- $$\frac{p}{T} = \frac{\partial S(E,V,N)}{\partial V}$$

$$= N k_B \cdot \frac{1}{V}$$

$$\Rightarrow \boxed{pV = N k_B T}$$

- $$\frac{\mu}{T} = -\frac{\partial S(E,V,N)}{\partial N}$$

$$= -k_B \left(\frac{3}{2} \ln E - \frac{3}{2} \ln N + \ln V + \tilde{\kappa} \right)$$

$$- N k_B \left(-\frac{3}{2}\right) \frac{1}{N}$$

$$= -k_B \left(\frac{3}{2} \ln E - \frac{3}{2} \ln N + \ln V - \frac{3}{2} + \tilde{\kappa} \right)$$

$$\Rightarrow \mu = k_B T \left(-\frac{3}{2} \ln E + \frac{3}{2} \ln N - \ln V + \frac{3}{2} - \tilde{\kappa} \right).$$

To completely determine μ, we need to know $\tilde{\kappa}$ – we will calculate it using quantum mechanics later in the course.

2 (a) $\quad G = E - TS + pV$

$$\Rightarrow \quad dG = dE - d(TS) + d(pV)$$

$$= dE - SdT - TdS + Vdp + pdV.$$

Substituting the statement of conservation of energy

$$dE = đW + đQ + \sum_i \mu_i dN_i$$

$$= -pdV + TdS + \sum_i \mu_i dN_i,$$

we get

$$dG = \cancel{-pdV} + \cancel{TdS} + \sum_i \mu_i dN_i$$

$$- SdT - \cancel{TdS} + Vdp + \cancel{pdV}$$

$$= -SdT + Vdp + \sum_i \mu_i dN_i$$

$\Rightarrow$ G is naturally a function of T, p and $\vec{N}$ as the change in G is determined by the change in T, p and $\vec{N}$ using only conservation of energy (i.e not using any equations of state, which are specific to a given system).

(b) From (a),

$$dG = -S\,dT + V\,dp + \sum_i \mu_i\,dN_i \quad \text{—}\ (*)$$

On the other hand, via the definition of partial derivatives

$$dG(T,p,N) = \frac{\partial G(T,p,\vec{N})}{\partial T}\,dT + \frac{\partial G(T,p,\vec{N})}{\partial p}\,dp + \sum_i \frac{\partial G(T,p,\vec{N})}{\partial N_i}\,dN_i \quad \text{—}\ (**)$$

Comparing the coefficient of dT, dp and dN_i in $(*)$ and $(**)$ give the three equations of state

$$\frac{\partial G(T,p,\vec{N})}{\partial T} = -S$$

$$\frac{\partial G(T,p,\vec{N})}{\partial p} = V$$

$$\frac{\partial G(T,p,\vec{N})}{\partial N_i} = \mu_i$$

3. $$S(E,V) = \frac{4}{3} a V^{\frac{1}{4}} E^{3/4}$$

(a) $$\frac{1}{T} = \frac{\partial S(E,V)}{\partial E}$$

$$= \frac{4}{3} a V^{1/4} \frac{3}{4} E^{-1/4}$$

$$= a V^{1/4} E^{-1/4}$$

$$\Rightarrow E^{1/4} = a V^{1/4} T$$

$$\Rightarrow E = a^4 V T^4$$

$\Rightarrow$ Energy density $\underline{\frac{E}{V} = a^4 T^4}$

(b) $$\frac{P}{T} = \frac{\partial S(E,V)}{\partial V}$$

$$= \frac{4}{3} a . \frac{1}{4} V^{-3/4} E^{3/4}$$

$$= \frac{1}{3} a \left(\frac{E}{V}\right)^{3/4}$$

$$= \frac{1}{3} a (a^4 T^4)^{3/4}$$ from a)

$$= \frac{1}{3} a . a^3 T^3$$

$$= \frac{1}{3} a^4 T^3$$

$$\Rightarrow \underline{p = \frac{1}{3} a^4 T^4}$$

(c) Free energy

$$F = E - TS$$

$$= a^4 V T^4 - T.\ \tfrac{4}{3} a V^{\frac{1}{4}} E^{3/4}$$

$$= a^4 V T^4 - T.\ \tfrac{4}{3} a V^{\frac{1}{4}} (a^4 V T^4)^{3/4}$$

using (a)

$$= a^4 V T^4 - \tfrac{4}{3} a V^{\frac{1}{4}}.\ T.a^3 V^{3/4}.\ T^3$$

$$= a^4 V T^4 - \tfrac{4}{3} a^4 V T^4$$

$$= -\tfrac{1}{3} a^4 V T^4$$

(d) $$-p = \frac{\partial F(T, V)}{\partial V}$$

$$= -\tfrac{1}{3} a^4 T^4$$

$\Rightarrow \quad p = \tfrac{1}{3} a^4 T^4$, consistent with (b).

(e) $$pV = \tfrac{1}{3} a^4 T^4 . V$$

From (a), $T^4 = \dfrac{E}{a^4 V}$

$$\Rightarrow \quad pV = \tfrac{1}{3} a^4 V \frac{E}{a^4 V}$$

$$= \tfrac{1}{3} E$$

(f) $\quad dE = đQ + đW$

For an adiabatic process, $đQ = 0$.

If the compression is quasistatic,

$đW = -p\,dV$

$\Rightarrow \quad dE = -p\,dV \quad$ —— (✱)

From (e), $\quad E = 3pV$.

Substituting into (✱)

$$3p\,dV + 3V\,dp = -p\,dV$$

$$\Rightarrow \quad 0 = 4p\,dV + 3V\,dp$$

Divide by $3pV$

$$0 = \frac{4}{3}\frac{dV}{V} + \frac{dp}{p}$$

$$= \frac{4}{3}\,d\ln V + d\ln p$$

$$= d\left(\ln V^{4/3} + \ln p\right)$$

$$= d\ln\left(pV^{4/3}\right)$$

$$\Rightarrow \quad \ln\left(pV^{4/3}\right) = \text{constant}$$

$$\Rightarrow \quad pV^{4/3} = \text{constant.}$$

(g) $G = E - TS + pV$

$= aVT^4 - T\,\frac{4}{3}aV^{\frac{1}{4}}\,(a^4VT^4)^{3/4} + \frac{1}{3}a^4VT^4$ using (a) and (e)

$= a^4VT^4 - \frac{4}{3}a^4VT^4 + \frac{1}{3}a^4VT^4$

$= 0.$

4. Equation of state

$$\frac{1}{T} = \frac{\partial S(E,A)}{\partial E}$$

$$S(E,A) = N k_B \left(\ln\left(\frac{mAE}{2\pi \hbar^2 N}\right) + 2 \right)$$

$$= 2N k_B + N k_B \ln E + N k_B \ln\left(\frac{mA}{2\pi \hbar^2 N}\right)$$

$$\Rightarrow \frac{\partial S(E,A)}{\partial E} = N k_B \frac{1}{E}$$

i.e. $\frac{1}{T} = N k_B \frac{1}{E}$

$$\Rightarrow \underline{E = N k_B T}$$

The equipartition theorem says there is $\frac{1}{2} k_B T$ of energy on average associated with each degree of freedom. Each atom in the gas has two degrees of freedom (motion in the x and y directions) $\Rightarrow$ average kinetic energy of $\frac{1}{2} k_B T$ in each of these directions

$\Rightarrow$ average energy of $k_B T$ per particle

$\Rightarrow$ energy $N k_B T$ for N particles

5 (a) Conservation of energy

$$dE = T\,dS - p\,dV + \sum_i{}' \mu_i\,dN_i \qquad -(*)$$

$\Rightarrow$ the change in the energy is determined by the changs in S, V and $\vec{N}$ for all systems

$\Rightarrow$ $E = E(S, V, \vec{N})$, the energy is "naturally" a function of S, V and $\vec{N}$

(b) Using the ~~par~~ definition of partial derivatives

$$dE(S,V,\vec{N}) = \frac{\partial E(S,V,\vec{N})}{\partial S}\,dS + \frac{\partial E(S,V,\vec{N})}{\partial V}\,dV + \sum_i \frac{\partial E(S,V,\vec{N})}{\partial N_i}\,dN_i \qquad -(**)$$

Comparing the coefficients of dS, dV and dN_i in (*) and (**) give the equations of state

$$T = \frac{\partial E(S,V,\vec{N})}{\partial S}$$

$$-p = \frac{\partial E(S,V,\vec{N})}{\partial V}$$

$$\mu_i = \frac{\partial E(S,V,\vec{N})}{\partial N_i}$$