MAU34405: Statistical Physics I
Homework 1 due 11/10/2021

Ruaidhrí Campion
19333850
JS Theoretical Physics

Exercise 1

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \qquad P = -\left(\frac{\partial E}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial E}{\partial N}\right)_{T,V}$$

$$T(S,V,N) = \frac{2a\,S}{N} \qquad P(S,V,N) = \frac{2b\,V}{N} \qquad \mu(S,V,N) = -\frac{a\,S^2}{N^2} + \frac{b\,V^2}{N^2}$$

$$\begin{aligned}
\mu &= -\frac{a\,S^2}{N^2} + \frac{b\,V^2}{N^2} \\
&= -\frac{1}{N}\left(a\,\frac{S^2}{N} - b\,\frac{V^2}{N}\right) \\
&= -\frac{E}{N}
\end{aligned}$$

Exercise 2

1.

The container in question is thermally and chemically isolated, and so no particles are exchanged between the inside of the container and the outside, i.e. the number of particles N is conserved in the process. Since we are told that the gas undergoes free expansion, and that the container is thermally isolated, we know that there is no work done on or by the container by or on the surroundings, and also that there is no heat flow between the container and the surroundings, i.e. $dQ = dW = 0$. From this we can deduce that energy E is conserved, since $dE = dQ + dW = 0 + 0 = 0$.

2.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad \text{(differential of } S(T,V))$$

$$C_V \equiv \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad \text{(alternative definition of specific heat capacity at constant volume)}$$

$$\begin{aligned}
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V && \text{(Maxwell's relations)} \\
&= \frac{k\,N}{V - b\,N} \\
\implies dS &= \frac{C_V}{T}\,dT + \frac{k\,N}{V - b\,N}\,dV && \text{(substituting)}
\end{aligned}$$

$$\begin{aligned}
dE &= T\,dS - P\,dV + \sum_i \mu_i\,dN_i && \text{(differential form of first law)} \\
&= C_V\,dT + \left(\frac{k\,N\,T}{V - b\,N} - P\right) dV + 0 && \text{(substituting, isolated } \implies dN_i = 0) \\
&= \frac{3}{2}\,k\,N\,dT + a\,\frac{N^2}{V^2}\,dV && \text{(substituting given expressions)} \\
\implies E &= \frac{3}{2}\,k\,N\,T - a\,\frac{N^2}{V} + f(N) && \text{(integrating)}
\end{aligned}$$

$$dE = dW + dQ = 0 + 0 = 0 \qquad \text{(free expansion \& thermally isolated)}$$

$$\implies E_{\text{initial}} = E_{\text{final}}$$

$$\implies \frac{3}{2}\,k\,N\,T_0 - a\,\frac{N^2}{\frac{1}{3}V_0} + f(N) = \frac{3}{2}\,k\,N\,T_F - a\,\frac{N^2}{V_0} + f(N)$$

$$\implies \frac{3}{2}\,k\,N\,T_0 - 3a\,\frac{N^2}{V_0} = \frac{3}{2}\,k\,N\,T_F - a\,\frac{N^2}{V_0}$$

$$\implies T_F = T_0 - \frac{4a\,N}{3k\,V_0}$$

Exercise 3

$$dE = T\,dS - P\,dV + \sum_i \mu_i\,dN_i$$

$$= \frac{3A\,S^2}{N\,V}\,dS - \frac{A\,S^3}{N\,V^2}\,dV + 0 \qquad \text{(assuming constant } N\text{)}$$

$$= \frac{A}{N}\,d\left(\frac{S^3}{V}\right)$$

$$\implies E(S,V,N) = \frac{A\,S^3}{N\,V} + f(N)$$

$$E(\lambda\,S, \lambda\,V, \lambda\,N) = \lambda\,E(S,V,N)$$

$$\implies \frac{\lambda^3\,A\,S^3}{\lambda^2\,N\,V} + f(\lambda\,N) = \frac{\lambda\,A\,S^3}{N\,V} + \lambda\,f(N)$$

$$\implies f(\lambda\,N) = \lambda\,f(N)$$

$$\implies f(N) = \alpha\,N, \quad \text{for some constant } \alpha$$

$$\implies E(S,V,N) = \frac{A\,S^3}{N\,V} + \alpha\,N$$

2.

$$T = \frac{3A\,S^2}{N\,V}, \quad P = \frac{A\,S^3}{N\,V^2}$$

$$\implies V = \frac{3A\,S^2}{N\,T}, \quad V^2 = \frac{A\,S^3}{N\,P}$$

$$\implies \left(\frac{3A\,S^2}{N\,T}\right)^2 = \frac{A\,S^3}{N\,P}$$

$$\implies S = \frac{N\,T^2}{9A\,P}$$

$$\implies V = \frac{N\,T^3}{27A\,P^2}$$

$$\implies d\mu = -\frac{T^2}{9A\,P}\,dT + \frac{T^3}{27A\,P^2}$$

$$= -\frac{1}{A}\,d\left(\frac{T^3}{27P}\right)$$

$$\implies \mu = -\frac{T^3}{27A\,P} + \mu_0$$

$$
\begin{aligned}
E &= T\,S - P\,V + \mu\,N \\
&= \frac{3A\,S^3}{N\,V} - \frac{A\,S^3}{N\,V} - \frac{N\,T^3}{27A\,P} + \mu_0 N \\
&= \frac{2A\,S^3}{N\,V} - \frac{N}{27A}\,\frac{27A^3\,S^6}{N^3\,V^3}\,\frac{N\,V^2}{A\,S^3} + \mu_0 N \\
&= \frac{2A\,S^3}{N\,V} - \frac{A\,S^3}{N\,V} + \mu_0 N \\
E(S,V,N) &= \frac{A\,S^3}{N\,V} + \mu_0 N \implies \alpha = \mu_0
\end{aligned}
$$

Exercise 4

$$
\begin{aligned}
dS &= \frac{1}{T}\,dE + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN \\
&= \frac{1}{\sqrt{a\,E^{\frac{3}{2}}\,V^{-1}\,N^{-\frac{1}{2}}}}\,dE + \frac{2E}{V\sqrt{a\,E^{\frac{3}{2}}\,V^{-1}\,N^{-\frac{1}{2}}}}\,dV + \qquad \text{(assuming constant } N\text{)} \\
&= a^{-\frac{1}{2}}\,E^{-\frac{3}{4}}\,V^{\frac{1}{2}}\,N^{\frac{1}{4}}\,dE + 2a^{-\frac{1}{2}}\,E^{\frac{1}{4}}\,V^{-\frac{1}{2}}\,N^{\frac{1}{4}}\,dV \\
&= a^{-\frac{1}{2}}\,N^{\frac{1}{4}}\,d\left(4E^{\frac{1}{4}}\,V^{\frac{1}{2}}\right) \\
\implies S(E,V,N) &= 4a^{-\frac{1}{2}}\,E^{\frac{1}{4}}\,V^{\frac{1}{2}}\,N^{\frac{1}{4}} + f(N)
\end{aligned}
$$

$$
\begin{aligned}
S(\lambda\,E,\lambda\,V,\lambda\,N) &= \lambda\,S(E,V,N) \\
\implies 4a^{-\frac{1}{2}}\,\lambda^{\frac{1}{4}}\,E^{\frac{1}{4}}\,\lambda^{\frac{1}{2}}\,V^{\frac{1}{2}}\,\lambda^{\frac{1}{4}}\,N^{\frac{1}{4}} + f(\lambda\,N) &= 4\lambda\,a^{-\frac{1}{2}}\,E^{\frac{1}{4}}\,V^{\frac{1}{2}}\,N^{\frac{1}{4}} + \lambda\,f(N) \\
\implies f(\lambda\,N) &= \lambda\,f(N) \\
\implies f(N) &= \beta\,N, \quad \text{for some constant } \beta \\
\implies S(E,V,N) &= 4a^{-\frac{1}{2}}\,E^{\frac{1}{4}}\,V^{\frac{1}{2}}\,N^{\frac{1}{4}} + \beta\,N
\end{aligned}
$$

Exercise 5

$$
\begin{aligned}
\left.\frac{\partial J}{\partial L}\right|_T &= \frac{a\,T}{L_0}\left[1 + 2\left(\frac{L_0}{L}\right)^3\right] \\
\implies J(T,L) &= a\,T\int\left(\frac{1}{L_0} + \frac{2a\,L_0^2}{L^3}\right)dL \\
&= a\,T\left(\frac{L}{L_0} - \frac{L_0^2}{L^2}\right) + f(T) \\
J(T,L_0) &= a\,T - a\,T + f(T) \\
&\equiv 0 \implies f(T) = 0 \\
\implies J(T,L) &= a\,T\left(\frac{L}{L_0} - \frac{L_0^2}{L^2}\right)
\end{aligned}
$$

$$
\begin{aligned}
dF &\equiv dE - T\,dS - S\,dT \\
&= J\,dL - S\,dT \qquad \text{(since } dE = T\,dS + J\,dL\text{)} \\
\implies J &= \left(\frac{\partial F}{\partial L}\right)_T, \quad -S = \left(\frac{\partial F}{\partial T}\right)_L
\end{aligned}
$$

$$\left(\frac{\partial J}{\partial T}\right)_L = \left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial L}\right)_T\right)_L$$
$$= \left(\frac{\partial}{\partial L}\left(\frac{\partial F}{\partial T}\right)_L\right)_T$$
$$= -\left(\frac{\partial S}{\partial L}\right)_T$$

$$dE \equiv T\,dS + J\,dL$$
$$\implies \left(\frac{\partial E}{\partial L}\right)_T = T\left(\frac{\partial S}{\partial L}\right)_T + J$$
$$= -T\left(\frac{\partial J}{\partial T}\right)_L + J$$
$$= -T\left(a\left(\frac{L}{L_0} - \frac{L_0^2}{L^2}\right)\right) + J$$
$$= -J + J = 0$$

$$dE = \left(\frac{\partial E}{\partial L}\right)_T dL + \left(\frac{\partial E}{\partial T}\right)_L dT$$
$$= 0 + C_L dT$$
$$\implies E(T) = C_L\,T + \alpha$$

Free expansion in adiabatic environment $\implies dE = 0$
$$\implies E(T_{\text{initial}}) = E(T_{\text{final}})$$
$$\implies C_L\,T_{\text{initial}} + \alpha = C_L\,T_{\text{final}} + \alpha$$
$$\implies T_{\text{initial}} = T_{\text{final}}$$

$$-\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial J}{\partial T}\right)_L$$
$$\implies S = a\int_{L_{\text{initial}}}^{L_0}\left(\frac{L_0^2}{L^2} - \frac{L}{L_0}\right) dL$$
$$= a\left(-\frac{L_0^2}{L} - \frac{L^2}{2L_0}\right)\Bigg|_{L_{\text{initial}}}^{L_0}$$
$$= a\left(-L_0 - \frac{L_0}{2} + \frac{L_0^2}{L_{\text{initial}}} + \frac{L_{\text{initial}}^2}{2L_0}\right)$$
$$S = a\,L_0\left(\frac{L_{\text{initial}}^2}{2L_0^2} + \frac{L_0}{L_{\text{initial}}} - \frac{3}{2}\right)$$
Label $f(x) \equiv \dfrac{x^2}{2} + \dfrac{1}{x}$
$$f\left(\frac{L_{\text{initial}}}{L_0}\right) = \frac{L_{\text{initial}}^2}{2L_0^2} + \frac{L_0}{L_{\text{initial}}}, \qquad f(1) = \frac{3}{2}$$
$$\implies S = a\,L_0\left(f\left(\frac{L_{\text{initial}}}{L_0}\right) - f(1)\right)$$

$$f'(1) = 1 - \frac{1}{1^2} = 0 \qquad\qquad f''(1) = 1 + \frac{1}{1^3} = 3 > 0$$

Thus f has a local minimum at $x = 1$. Since $f \to \infty$ as $x \to 0$ and $x \to \infty$, $x = 1$ is a global minimum for positive x. Thus for any $L_{\text{initial}} \neq L_0$ we have that $f\left(\frac{L_{\text{initial}}}{L_0}\right) > f(1)$. Since a and L_0 are positive constants, we must also have $S = a\,L_0\left(f\left(\frac{L_{\text{initial}}}{L_0}\right) - f(1)\right) > 0$, and thus the entropy increases in this process.

Exercise 6

$$
\begin{aligned}
P\,V^k = a \implies P &= a\,V^{-k} \\
\text{Also, } P &= -\left(\frac{\partial E}{\partial V}\right)_{S,N} \\
\implies dE|_{S,N} &= -a\,V^{-k}\,dV \\
\implies E &= -\frac{a\,V^{-k+1}}{-k+1} + f_1(S,N) \\
&= \frac{P\,V}{k-1} + f_2\!\left(\frac{S}{N}, N\right)
\end{aligned}
$$

$$
\begin{aligned}
E\!\left(P, \lambda\,V, \frac{S}{N}, \lambda\,N\right) &= \lambda\,E\!\left(P, V, \frac{S}{N}, N\right) \\
\implies \frac{\lambda\,P\,V}{k-1} + f_2\!\left(\frac{S}{N}, \lambda\,N\right) &= \frac{\lambda\,P\,V}{k-1} + \lambda\,f_2\!\left(\frac{S}{N}, N\right) \\
\implies f_2\!\left(\frac{S}{N}, N\right) &= N\,f_3\!\left(\frac{S}{N}\right)
\end{aligned}
$$

$$
\begin{aligned}
P\,V^k &= a(S,N) \\
&= f_4\!\left(\frac{S}{N}, N\right) \\
P\,(\lambda\,V)^k &= \lambda^k\,P\,V^k \\
&= \lambda^k\,f_4\!\left(\frac{S}{N}, N\right) \\
\implies f_4\!\left(\frac{S}{N}, N\right) &= N^k\,f_5\!\left(\frac{S}{N}\right) \\
\implies f_5\!\left(\frac{S}{N}\right) &= \frac{P\,V^k}{N^k} \\
\implies \frac{S}{N} &= f_5^{-1}\!\left(\frac{P\,V^k}{N^k}\right)
\end{aligned}
$$

$$
\begin{aligned}
\implies E &= \frac{P\,V}{k-1} + N\,f_3\!\left(f_5^{-1}\!\left(\frac{P\,V^k}{N^k}\right)\right) \\
&= \frac{P\,V}{k-1} + N\,f\!\left(\frac{P\,V^k}{N^k}\right) \qquad \text{(where } f \equiv f_3 \circ f_5^{-1}\text{)}
\end{aligned}
$$