Final - Statistical Physics

Winter Quarter 2004

1. Two identical ideal gases at pressures P_1 and P_2 and temperatures T_1 and T_2 are in vessels of volumes V_1 and V_2 respectively. The vessels are then connected and gases mix. Find the change of entropy after the system reaches equilibrium. (The system as a whole can be considered as thermally isolated.) Simplify your answer for the cases: a) $P_1 = P_2$ and $V_1 = V_2$; b) $T_1 = T_2$ and $V_1 = V_2$. **Bonus question**: For both a) and b) explicitly show that the change of entropy is greater or equal than zero.

   Hint: $S = -N \log P + N c_p \log T + (\zeta + c_p) N$

   Solution

   Number of particles in the vessels

$$N_{1,2} = \frac{P_{1,2} V_{1,2}}{T_{1,2}}$$

   Final T and P ($V = V_1 + V_2$)

$$\begin{aligned}
E &= (N_1 + N_2) T = E_1 + E_2 = N_1 T_1 + N_2 T_2 \\
T &= \frac{N_1 T_1 + N_2 T_2}{N_1 + N_2} = \frac{P_1 V_1 + P_2 V_2}{(P_1 V_1 / T_1) + (P_2 V_2 / T_2)} \\
P &= \frac{(N_1 + N_2) T}{V_1 + V_2} = \frac{P_1 V_1 + P_2 V_2}{V_1 + V_2}
\end{aligned}$$

   Initial entropy

$$\begin{aligned}
S_0 &= S_1 + S_2 \\
&= -N_1 \log P_1 + N_1 c_p \log T_1 - N_2 \log P_2 + N_2 c_p \log T_2 \\
&\quad + (\zeta + c_p)(N_2 + N_1)
\end{aligned}$$

   Final entropy

$$S = -(N_2 + N_1) \log P + (N_2 + N_1) c_p \log T + (\zeta + c_p)(N_2 + N_1)$$

Change of entropy

$$\begin{aligned}\Delta S &= S - S_0 \\ &= -\left[N_1 \log \frac{P}{P_1} + N_2 \log \frac{P}{P_2}\right] + c_p \left[N_1 \log \frac{T}{T_1} + N_2 \log \frac{T}{T_2}\right]\end{aligned}$$

a) $P_1 = P_2$ and $V_1 = V_2$

$$\begin{aligned}P &= P_1 = P_2 \\ T &= \frac{2T_1T_2}{T_1 + T_2}\end{aligned}$$

$$\Delta S = c_p \left(N_1 \log \frac{T}{T_1} + N_2 \log \frac{T}{T_2}\right) = \frac{c_p pV}{2} \left(\frac{1}{T_1} \log \frac{T}{T_1} + \frac{1}{T_2} \log \frac{T}{T_2}\right)$$

Using notation $T_2 = T_1 - \Delta T$, $\Delta T \geq 0$, and $0 \leq x = \Delta T/T_1 \leq 1$,

$$\begin{aligned}\frac{T}{T_1} &= \frac{2\left(T_1 - \Delta T\right)}{2T_1 - \Delta T} = \frac{1 - x}{1 - x/2} \\ \frac{T}{T_2} &= \frac{2T_1}{2T_1 - \Delta T} = \frac{1}{1 - x/2}\end{aligned}$$

$$\Delta S = \frac{c_p pV}{2T_2} \left(\frac{T_2}{T_1} \log \frac{T}{T_1} + \log \frac{T}{T_2}\right) = \frac{c_p pV}{2T_2} \left[(1 - x) \log \frac{1 - x}{1 - x/2} + \log \frac{1}{1 - x/2}\right] \geq 0$$

Equality is achieved when $x = 0$, that is $T_2 = T_1$.

b) $T_1 = T_2$ and $V_1 = V_2$

$$\begin{aligned}T &= T_1 = T_2 \\ P &= \frac{P_1 + P_2}{2}\end{aligned}$$

$$\Delta S = S - S_0 = -\left[N_1 \log \frac{P}{P_1} + N_2 \log \frac{P}{P_2}\right] = -\frac{V}{2T} \left[P_1 \log \frac{P}{P_1} + P_2 \log \frac{P}{P_2}\right]$$

Using notation $P_2 = P_1 - \Delta P$, $\Delta P \geq 0$, and $0 \leq x = \Delta P/P_1 \leq 1$,

$$\begin{aligned}\frac{P}{P_1} &= \frac{2P_1 - \Delta P}{2P_1} = 1 - x/2 \\ \frac{P}{P_2} &= \frac{2P_1 - \Delta P}{P_1 - \Delta P} = \frac{1 - x/2}{1 - x}\end{aligned}$$

$$\Delta S = -\frac{VP_1}{2T}\left[\log\frac{P}{P_1} + \frac{P_2}{P_1}\log\frac{P}{P_2}\right] = -\frac{VP_1}{2T}\left[\log\left(1 - x/2\right) + (1-x)\log\left(\frac{1-x/2}{1-x}\right)\right] \geq 0$$

Equality is achieved when $x = 0$, that is $P_2 = P_{1.}$

2. A one-dimensional harmonic oscillator, $\varepsilon_n = \hbar\omega\,(n + 1/2)$, $n \geq 0$, is in thermal equilibrium with a heat bath at temperature T. Evaluate

   a) The mean value of the oscillator energy $\langle E \rangle$;

   b) The root mean square fluctuation of energy about $\langle E \rangle$, $\left\langle (\Delta E)^2 \right\rangle^{1/2} = \sqrt{C_v}T$.

   What is the behavior of $\langle E \rangle$ and $\left\langle (\Delta E)^2 \right\rangle^{1/2}$ in the limits of high and low temperature?

   Solution

   Partition function

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} \exp\left[\frac{-\hbar\omega\,(n+1/2)}{T}\right] \\ &= \exp\left(-\frac{\hbar\omega}{2T}\right)\left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right]^{-1} = \frac{2}{\sinh\left(\hbar\omega/2T\right)} \end{aligned}$$

   Energy

$$\begin{aligned} \langle E \rangle &= F - T\frac{\partial F}{\partial T} = T^2 Z^{-1}\frac{\partial Z}{\partial T} \\ &= \frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2T}\right) = \begin{matrix} \hbar\omega/2,\ T \ll \hbar\omega \\ T,\ T \gg \hbar\omega \end{matrix} \end{aligned}$$

   Heat capacity

$$C_v = \frac{\partial\langle E \rangle}{\partial T} = \frac{\left(\hbar\omega/2T\right)^2}{\sinh^2\left(\hbar\omega/2T\right)}$$

   Energy. fluctuation

$$\begin{aligned} \left\langle (\Delta E)^2 \right\rangle^{1/2} &= \sqrt{C_v}T = \frac{\hbar\omega/2}{\sinh\left(\hbar\omega/2T\right)} \\ &= \begin{matrix} (\hbar\omega/2)\exp\left(-\hbar\omega/2T\right),\ T \ll \hbar\omega \\ T,\ T \gg \hbar\omega \end{matrix} \end{aligned}$$