Pongpak Techagumthorn Phys 224: Thermal Physics

HW 3

2.24 (a)

$$\begin{aligned}
\Omega\left(N, \frac{N}{2}\right) &= \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \\
&\approx \frac{N^N E^{-N}\sqrt{2\pi N}}{\left(\left(\frac{N}{2}\right)^{(N/2)} E^{-(N/2)}\sqrt{\pi N}\right)\left(\left(\frac{N}{2}\right)^{(N/2)} E^{-(N/2)}\sqrt{\pi N}\right)} \\
&\approx \frac{N^N E^{-N}\sqrt{2\pi N}}{\left(\frac{N}{2}\right)^N E^{-N}\pi N} \\
&\approx \frac{2^N\sqrt{2\pi N}}{\pi N} \\
&\approx \frac{2^{N+1}}{\sqrt{2\pi N}} \\
&\approx \frac{2^{N+\frac{1}{2}}}{\sqrt{2\pi}} \\
\Omega_{max} &\approx 2^N
\end{aligned}$$

(b)

$$x \equiv N\uparrow - \frac{N}{2}$$

$$N\uparrow = \frac{N}{2} + 2$$

$$\begin{aligned}
N &= N\uparrow + N\downarrow \\
N &= \frac{N}{2} + x + N\downarrow \\
\frac{N}{2} &= x + N\downarrow \\
N\downarrow &= \frac{N}{2} - x
\end{aligned}$$

$$\Omega = \binom{N\downarrow + N\uparrow + 1}{N\downarrow} = \binom{\frac{N}{2} + x + \frac{N}{2} - x + 1}{\frac{N}{2} - x}$$

$$
\begin{aligned}
\Omega &\approx \binom{N}{\frac{N}{2}-x} = \frac{N!}{\left(\frac{N}{2}-x\right)!\left(\frac{N}{2}-x\right)!} \\
&\approx \frac{N^N e^{-N}\sqrt{2\pi N}}{\left(\left(\frac{N}{2}-x\right)^{\left(\frac{N}{2}-x\right)} e^{-(\frac{N}{2}-x)}\sqrt{2\pi(\frac{N}{2}-x)}\right)\left(\left(\frac{N}{2}+x\right)^{\left(\frac{N}{2}+x\right)} e^{-(\frac{N}{2}+x)}\sqrt{2\pi(\frac{N}{2}+x)}\right)} \\
&\approx \frac{N^N\sqrt{2\pi N}}{\left(\left(\frac{N}{2}-x\right)^{\left(\frac{N}{2}-x\right)}\sqrt{2\pi(\frac{N}{2}-x)}\right)\left(\left(\frac{N}{2}+x\right)^{\left(\frac{N}{2}+x\right)}\sqrt{2\pi(\frac{N}{2}+x)}\right)} \\
&\approx \frac{N^N\sqrt{2\pi N}}{2\pi\sqrt{(\frac{N}{2})^2-x^2}\left(\frac{N}{2}-x\right)^{\left(\frac{n}{2}-x\right)}\left(\frac{N}{2}+x\right)^{\left(\frac{N}{2}+x\right)}} \\
&\approx \frac{N^N\sqrt{2\pi N}}{2\pi\sqrt{(\frac{N}{2})^2-x^2}\left(\frac{N}{2}-x\right)^{\frac{N}{2}}\left(\frac{N}{2}-x\right)^{-x}\left(\frac{N}{2}+x\right)^{\frac{N}{2}}\left(\frac{N}{2}+x\right)^{x}} \\
&\approx \frac{N^N\sqrt{2\pi N}}{2\pi\sqrt{(\frac{N}{2})^2-x^2}\left(\left(\frac{N}{2}\right)^2-x^2\right)^{\frac{N}{2}}\left(\frac{N}{2}-x\right)^{-x}\left(\frac{N}{2}+x\right)^{x}} \\
&\approx \frac{N^N\sqrt{N}}{\sqrt{2\pi(\frac{N}{2})^2-x^2}\left(\left(\frac{N}{2}\right)^2-x^2\right)^{\frac{N}{2}}\left(\frac{N}{2}-x\right)^{-x}\left(\frac{N}{2}+x\right)^{x}} \\
\Omega &\approx \frac{N^N}{\left(\left(\frac{N}{2}\right)^2-x^2\right)^{\frac{N}{2}}\left(\frac{N}{2}-x\right)^{-x}\left(\frac{N}{2}+x\right)^{x}} \\
\ln(\Omega) &\approx \ln\left(\frac{N^N}{\left(\left(\frac{N}{2}\right)^2-x^2\right)^{\frac{N}{2}}\left(\frac{N}{2}-x\right)^{-x}\left(\frac{N}{2}+x\right)^{x}}\right) \\
&\approx \ln(N^N) - \ln\left(\left(\left(\frac{N}{2}\right)^2-x^2\right)^{N/2}\right) - \ln\left(\left(\frac{N}{2}-x\right)^{-x}\right) - \ln\left(\left(\frac{N}{2}+x\right)^{x}\right) \\
&\approx N\ln(N) - \frac{N}{2}\ln\left(\left(\frac{N}{2}\right)^2-x^2\right) + x\ln\left(\frac{N}{2}-x\right) - x\ln\left(\frac{N}{2}+x\right)
\end{aligned}
$$

i.

$$
\begin{aligned}
\frac{N}{2}\ln\left(\left(\frac{N}{2}\right)^2 - x^2\right) &= \frac{N}{2}\ln\left(\left(\frac{N}{2}\right)^2\left(1-\left(\frac{2x}{N}\right)^2\right)\right) \\
&= \frac{N}{2}\ln\left(\left(\frac{N}{2}\right)^2\right) + \frac{N}{2}\ln\left(1-\left(\frac{2x}{N}\right)^2\right) \\
&= N\ln\left(\frac{N}{2}\right) - \frac{N}{2}\left(\frac{2x}{N}\right)^2 \\
&= N\ln(N) - N\ln(2) - \frac{2x^2}{N}
\end{aligned}
$$

ii.

$$
\begin{aligned}
x\ln\left(\frac{N}{2} - x\right) &= x\ln\left(\frac{N}{2}\left(1-\frac{2x}{N}\right)\right) \\
&= x\ln\left(\frac{N}{2}\right) + x\ln\left(1-\frac{2x}{N}\right) \\
&= x\ln\left(\frac{N}{2}\right) - x\left(\frac{2x}{N}\right) \\
&= x\ln\left(\frac{N}{2}\right) - \frac{2x^2}{N}
\end{aligned}
$$

iii.

$$
\begin{aligned}
x\ln\left(\frac{N}{2} + x\right) &= x\ln\left(\frac{N}{2}\left(1+\frac{2x}{N}\right)\right) \\
&= x\ln\left(\frac{N}{2}\right) + x\ln\left(1+\frac{2x}{N}\right) \\
&= x\ln\left(\frac{N}{2}\right) + x\left(\frac{2x}{N}\right) \\
&= x\ln\left(\frac{N}{2}\right) + \frac{2x^2}{N}
\end{aligned}
$$

$$
\begin{aligned}
\ln(\Omega) &\approx N\ln(N) - \left(N\ln(N) - N\ln(2) - \frac{2x^2}{N}\right) + \left(x\ln\left(\frac{N}{2}\right) - \frac{2x^2}{N}\right) - \left(x\ln\left(\frac{N}{2}\right) + \frac{2x^2}{N}\right) \\
\ln(\Omega) &\approx N\ln(2) - \frac{2x^2}{N} \\
\Omega &\approx 2^N e^{-\frac{2x^2}{N}} \\
\Omega &\approx 2^N \quad (\Omega_{max}, x = 0)
\end{aligned}
$$

(c) Width measured when value falls to $\frac{1}{e}$ of max value.

$$\frac{\Omega_{max}}{e} = \Omega_{max} e^{-\frac{2x^2}{N}}$$
$$e^{-1} = e^{-\frac{2x^2}{N}}$$
$$1 = \frac{2x^2}{N}$$
$$x^2 = \frac{N}{2}$$
$$x = \sqrt{\frac{N}{2}}$$

Total width $w = 2x = 2\sqrt{\frac{N}{2}} = \sqrt{2N}$.

(d)

$$P = \frac{\Omega}{\Omega_{max}} = \frac{\Omega_{max} e^{-\frac{2x^2}{N}}}{\Omega_{max}} = e^{-\frac{2x^2}{N}}$$
$$P_{501000} = e^{-\frac{2(1000)^2}{1000000}} = 0.135$$

501000 heads is probable

$$P_{510000} = e^{-\frac{2(10000)^2}{1000000}} = 1.38 \times 10^{-87}$$

510000 heads is improbable

2.25 (a) N = Total Steps, n = Steps away from starting position

$$\Omega \approx \frac{N!}{n!(N-n)!}$$
$$\Omega_{max} \approx 2^N$$
$$P = \frac{\Omega}{\Omega_{max}} = \frac{N!}{n!(N-n)!}\frac{1}{2^N}$$

Highest probability state is when $n = 0$, so ending up at the same place. It is also probable that you will end up in a spot that is within the width of the peak, so $\pm\sqrt{\frac{N}{2}}$ steps away from the starting position.

(b) max $\Delta x = \pm\sqrt{\frac{10000}{2}} \approx \pm 71$.
It is likely that you will end up within ± 71 steps from the starting point.

(c) Mean free path:

$$\ell = \frac{1}{4\pi r^2}\frac{V}{N_{mol}}$$
$$\overline{v} = \sqrt{\frac{3kT}{m}}$$

Typical values for air at STP: $\ell = 1.5 \times 10^{-7}m$ and $\overline{v} = 500m/s$.

$$N = \frac{\overline{v}t}{\ell}$$

$$\begin{aligned}
\Delta x &\approx x_{width}\ell = \sqrt{\frac{N}{2}}\ell = \sqrt{\frac{\overline{v}t}{2l}}\ell \\
&\approx \sqrt{\frac{\overline{v}t\ell}{2}} \\
\Delta x &\approx \sqrt{\frac{(500)(1)(1.5 \times 10^{-7})}{2}} = 0.0061m
\end{aligned}$$

Δx depends on $\sqrt{t}$ so for an increasing Δx the time it takes will grow at an exponential rate.
Δx also has a dependence on $\sqrt[4]{T}$ so for increases in temperature Δx does not appreciably change.

2.29

$$\begin{aligned}
\Omega_{most} &= 6.87 \times 10^{114} \\
\Omega_{least} &= 2.77 \times 10^{81} \\
S_{most} &= \ln(\Omega_{most}) = \ln(6.87 \times 10^{114}) = 264.4 \\
S_{least} &= \ln(\Omega_{least}) = \ln(2.77 \times 10^{81}) = 187.5 \\
\Omega_{total} &= 9.26 \times 10^{115} \\
S_{total} &= \ln(\Omega_{total}) = \ln(9.26 \times 10^{115}) = 267
\end{aligned}$$

2.34

$$\begin{aligned}
S &= k\ln(\Omega) \\
&= Nk\left[\ln\left(\frac{V}{N}\left(\frac{4n\pi U}{3Nh^3}\right)^{\frac{3}{2}}\right) + \frac{5}{2}\right] \quad DoF = 3
\end{aligned}$$

$$\begin{aligned}
Q &= \Delta U + W \quad \Delta U = 0 \\
&= W = \int_{V_i}^{V_f} PdV \quad P = \frac{NkT}{V} \\
&= NkT\int_{V_i}^{V_f} \frac{dV}{V} = NkT\ln\left(\frac{V_f}{V_i}\right)
\end{aligned}$$

$$\begin{aligned}
S &= Nk\left[\ln\left(\frac{V}{N}\left(\frac{4n\pi U}{3Nh^3}\right)^{\frac{3}{2}} + \frac{5}{2}\right)\right] \\
&= Nk\left[\ln(V)\ln\left(\frac{1}{N}\left(\frac{4n\pi U}{3Nh^3}\right)^{\frac{3}{2}}\right) + \frac{5}{2}\right]
\end{aligned}$$

$\ln\left(\frac{1}{N}\left(\frac{4n\pi U}{3Nh^3}\right)^{\frac{3}{2}}\right)+\frac{5}{2}$ is constant

$$\Delta S = Nk\ln(V_f) - Nk\ln(V_i) = Nk\ln\left(\frac{V_f}{V_i}\right)$$
$$= Nk\ln\left(\frac{V_f}{V_i}\right)\frac{T}{T} = \frac{NkT\ln\left(\frac{V_f}{V_i}\right)}{T}$$
$$\Delta S = \frac{Q}{T}$$

2.36

$$S \approx Nk$$
$$N_{book} = \frac{1000}{12} \times 6.022 \times 10^{22} = 5.02 \times 10^{25}$$
$$S_{book} = 5.02 \times 10^{25} \times 1.38 \times 10^{-23} = 693JK^{-1}$$
$$N_{moose} = \frac{400 \times 10^3}{18} \times 6.022 \times 10^{22} = 1.34 \times 10^{28}$$
$$S_{moose} = 1.34 \times 10^{28} \times 1.38 \times 10^{-23} = 1.84 \times 10^5 JK^{-1}$$
$$N_{sun} = \frac{2 \times 10^{33}}{12} \times 6.022 \times 10^{22} = 1.2 \times 10^{57}$$
$$S_{sun} = 1.2 \times 10^{57} \times 1.38 \times 10^{-23} = 1.66 \times 10^{34} JK^{-1}$$

3.1

$$\frac{1}{T} = \frac{\partial S}{\partial U}$$
$$T = \frac{\partial U}{\partial S} = \frac{\Delta U}{\Delta S} = \frac{\epsilon \Delta q}{\Delta S}$$
$$\epsilon = 0.1eV = 1.6 \times 10^{-20} J$$

(a) $q_a = 1$

$$T_A = \frac{\epsilon(2-0)}{S_A(2) - S_A(0)} = \frac{2\epsilon}{k(10.7-0)} = 0.187\frac{\epsilon}{k}$$
$$= 0.187\left(\frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}}\right) = 216.7K$$

$$T_B = \frac{\epsilon(100-98)}{S_B(100) - S_B(98)} = \frac{2\epsilon}{k(187.53 - 185.33)} = 0.909\frac{\epsilon}{k}$$
$$= 0.909\left(\frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}}\right) = 1054K$$

(b) $q_a = 60$

$$T_A = \frac{\epsilon(61-59)}{S_A(61)-S_A(59)} = \frac{2\epsilon}{k(160.9-157.35)} = 0.56\frac{\epsilon}{k}$$
$$= 0.56\left(\frac{1.6\times 10^{-20}}{1.38\times 10^{-23}}\right) = 649K$$

$$T_B = \frac{\epsilon(41-39)}{S_B(41)-S_B(39)} = \frac{2\epsilon}{k(107.0-103.5)} = 0.56\frac{\epsilon}{k}$$
$$= 0.56\left(\frac{1.6\times 10^{-20}}{1.38\times 10^{-23}}\right) = 649K$$
$$T_A = T_B$$

3.2

$$\frac{1}{T} = \frac{\partial S}{\partial U} \Rightarrow T = \frac{\partial U}{\partial S}$$
$$T_A = \frac{\partial U_A}{\partial S_A} \quad T_B = \frac{\partial U_B}{\partial S_B} \quad T_C = \frac{\partial U_C}{\partial S_C}$$

$$T_A = T_B$$
$$\frac{\partial U_A}{\partial S_A} = \frac{\partial U_B}{\partial S_B}$$
$$T_B = T_C$$
$$\frac{\partial U_B}{\partial S_B} = \frac{\partial U_C}{\partial S_C} \Rightarrow \frac{\partial U_A}{\partial S_A} = \frac{\partial U_C}{\partial S_C} \Rightarrow T_A = T_C$$

3.3 The two objects will exchange thermal energy until the slopes of their entropy vs energy graphs are equal.

3.5

$$\frac{1}{T} = \frac{\partial S}{\partial U} \quad \Omega = \left(\frac{Ne}{q}\right)^q$$
$$U = q\epsilon \Rightarrow q = \frac{U}{\epsilon}$$
$$\Omega = \left(\frac{Ne\epsilon}{U}\right)^{\frac{U}{\epsilon}}$$

$$
\begin{aligned}
S = k\ln(\Omega) &= k\ln\left[\left(\frac{Ne\epsilon}{U}\right)^{\frac{U}{\epsilon}}\right] \\
&= \frac{Uk}{\epsilon}\ln\left(\frac{Ne\epsilon}{U}\right) \\
&= \frac{Uk}{\epsilon}(\ln(N\epsilon) + \ln(e) - \ln(U)) \\
\frac{1}{T} = \frac{\partial S}{\partial U} &= \frac{\partial}{\partial U}\left[\frac{Uk}{\epsilon}(\ln(N\epsilon) + 1 - \ln(U))\right] \\
&= \frac{\partial}{\partial U}\left[\frac{Uk}{\epsilon}\ln(N\epsilon) + \frac{Uk}{\epsilon} - \frac{Uk}{\epsilon}\ln(U)\right] \\
&= \frac{k}{\epsilon}\ln(N\epsilon) + \frac{k}{\epsilon} - \left(\frac{k}{\epsilon}\ln(U) + \frac{Uk}{U\epsilon}\right) \\
\frac{1}{T} &= \frac{k}{\epsilon}(\ln(N\epsilon) - \ln(U)) \\
\frac{\epsilon}{kT} &= \ln(N\epsilon) - \ln(U) \\
e^{\ln(U)} &= e^{\left(\ln(N\epsilon) - \frac{\epsilon}{kT}\right)} \\
U &= N\epsilon e^{-\frac{\epsilon}{kT}}
\end{aligned}
$$

3.10 (a) Heat of formation for water $L_{H_20(\ell)} = 334Jg^{-1}$

$$Q = mL = (30)(334) = 10020J$$

$$\Delta S_A = \frac{Q}{T} = \frac{10020}{273} = 36.7JK^{-1}$$

(b)

$$c_{H_2O(\ell)} = 4.181Jg^{-1}K^{-1}$$

$$\Delta S_B = C_V\int_{T_i}^{T_f}\frac{1}{T}dT$$

$$C_V = mc$$

$$
\begin{aligned}
\Delta S_B &= mc\int_{T_i}^{T_f}\frac{1}{T}dT \\
&= mc\ln\left(\frac{T_f}{T_i}\right) \\
&= (30)(4.181)\ln\left(\frac{298}{273} = 11JK^{-1}\right)
\end{aligned}
$$

$$\Delta S_{water} = \Delta S_A + \Delta S_B = 36.7 + 11 = 47.7JK^{-1}$$

(c)

$$\begin{aligned} Q &= Q_{ice} + Q_{water} = Q_{ice} + mc\Delta T \\ &= 10020 + (30)(4.181)(25) = 13156J \end{aligned}$$

$$\Delta S_{room} = \frac{-13156}{298} = -44.7JK^{-1}$$

(d)

$$\Delta S_{univ} = \Delta S_{room} + \Delta S_{water} = -44.1 + 47.7 = 3.6JK^{-1}$$

A positive entropy is expected since the reaction occurs spontaneously

3.11

$$T_1 = 55C = 328K \quad T_2 = 10C = 283K \quad V_1 = 50L \quad V_2 = 25L$$

$$\begin{aligned} T_f &= \frac{T_1V_1 + T_2V_2}{V_1 + V_1} \\ &= \frac{(328)(50) + (283)(25)}{50 + 25} = 313K \end{aligned}$$

$$\Delta S = C_V \int_{T_i}^{T_f} \frac{1}{T} dT = C_v \ln\left(\frac{T_f}{T_i}\right) = mc \ln\left(\frac{T_f}{T_i}\right)$$

$$\Delta S_{hot} = (50000)(4.181) \ln\left(\frac{313}{328}\right) = -9786JK^{-1}$$

$$\Delta S_{cold} = (25000)(4.181) \ln\left(\frac{313}{283}\right) = 10532JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{hot} + \Delta S_{cold} = -9786 + 10532 = 746JK^{-1}$$

3.13 (a)

$$\Delta S = \frac{Q}{T} \quad Q = F_S T$$

$$F_s = 1000Wm^{-2} \quad t = 365 \times 8 \times 60 \times 60 = 10512000s$$

$$Q = (1000)(10512000) = 1.0512 \times 10^{10}$$

$$\Delta S_{\oplus} = \frac{1.0512 \times 10^{10}}{300} = 3.5 \times 10^7 JK^{-1}$$

$$\Delta S_{\odot} = \frac{-1.0512 \times 10^{10}}{6000} = -1.75 \times 10^6 JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{\oplus} + \Delta S_{\odot} = 3.5 \times 10^7 - 1.75 \times 10^6 = 3.325JK^{-1}$$

(b) In order for the grass to grow it needs sunlight. The entropy that is gained in the 1 square meter of grass is many magnitudes higher than the entropy lost in the formation of complex hydrocarbons.

3.14

$$C_V = aT + bT^3 \quad a = 0.00135 \quad b = 2.48 \times 10^{-5}$$

$$S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_V(T)}{T} dT$$
$$S(T_f) - S(0) = \int_0^{T_f} (a + bT^2) dT$$
$$S(T_f) = \left(aT + \frac{bT^3}{3} \right) \Bigg|_{T=0}^{T=T_f}$$
$$S(T_f) = aT_f + \frac{bT_f^2}{3}$$

$$S(1) = (0.00135)(1) + \frac{2.48 \times 10^{-5}}{3}(1)^3 = 1.36 \times 10^{-3} JK^{-1}$$
$$\frac{S(1)}{k} = \frac{1.36 \times 10^{-3}}{1.38 \times 10^{-23}} = 9.86 \times 10^{19}$$

$$S(10) = (0.00135)(10) + \frac{2.48 \times 10^{-5}}{3}(10)^3 = 2.18 \times 10^{-2} JK^{-1}$$
$$\frac{S(10)}{k} = \frac{2.18 \times 10^{-2}}{1.38 \times 10^{-23}} = 1.58 \times 10^{21}$$