

1. Problem 1:

(a)

$$L_x = L_y = L_z = (V - B)^{1/3} \Rightarrow L_x^2 = L_y^2 = L_z^2 = (V - B)^{2/3}$$

$$V(x, y, z) = -u_0$$

$$\hat{H}\psi(x, y, z) = E\psi(x, y, z)$$

$$\psi_{n_x, n_y, n_z}(x, y, z) = \psi_{n_x} \psi_{n_y} \psi_{n_z}$$

$$E_{n_x, n_y, n_z} = E_{n_x} + E_{n_y} + E_{n_z} = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right); \text{ when } V = 0$$

$$E_{n_x, n_y, n_z} = \left( \frac{n_x^2 \hbar^2 \pi^2}{2m(V - B)^{2/3}} + \frac{n_y^2 \hbar^2 \pi^2}{2m(V - B)^{2/3}} + \frac{n_z^2 \hbar^2 \pi^2}{2m(V - B)^{2/3}} \right) - u_0; \text{ when } V = -u_0$$

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m(V - B)^{2/3}} (n_x^2 + n_y^2 + n_z^2) - u_0$$

(b)

$$\begin{aligned}
E_{\text{trans}} &= E_{\text{trans}}^{\circ} - u_0 \\
z_{\text{trans}}(T) &= \sum e^{-\beta E_{\text{trans}}} = \sum e^{-\beta(E_{\text{trans}}^{\circ} - u_0)} = \sum e^{-\beta E_{\text{trans}}^{\circ} + \beta u_0} \\
&= \sum e^{-\beta E_{\text{trans}}^{\circ}} e^{\beta u_0} = e^{\beta u_0} \sum e^{-\beta E_{\text{trans}}^{\circ}}
\end{aligned}$$

$$\text{if } E_{\text{trans}}^{\circ}(n_x, n_y, n_z) = \frac{\pi^2 \hbar^2}{2m(V-B)^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$

$$z_{\text{trans}}(T) = e^{\beta u_0} \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta E_{\text{trans}}^{\circ}}$$

$$\text{let } \omega = \beta \frac{\pi^2 \hbar^2}{2m(V-B)^{2/3}}$$

$$\begin{aligned}
\text{then } z_{\text{trans}}(T) &= e^{\beta u_0} \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} (e^{-\omega n_x^2})(e^{-\omega n_y^2})(e^{-\omega n_z^2}) \\
&\simeq \frac{e^{\beta u_0}}{8} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} dn_x dn_y dn_z e^{-\omega n_x^2} e^{-\omega n_y^2} e^{-\omega n_z^2} \\
&= \frac{e^{\beta u_0}}{8} \left( \sqrt{\frac{\pi}{\omega}} \right)^3 = \frac{e^{\beta u_0}}{8} \left( \sqrt{\frac{\pi 2m(V-B)^{2/3}}{\beta \pi^2 \hbar^2}} \right)^3 \\
&= \frac{e^{\beta u_0}}{8} \left( \sqrt{\frac{2m(V-B)^{2/3} k_B T}{\pi \hbar^2}} \right)^3 \\
\text{therefore } z_{\text{trans}}(T) &= \frac{e^{\beta u_0}}{8} \left( \frac{2m k_B T}{\pi \hbar^2} \right)^{3/2} (V-B)
\end{aligned}$$

(c)

$$\begin{aligned}
P_k(T, V, \{N\}) &= P(E_k) = e^c e^{-\beta E_k} \\
\sum_k P_k(T, V, \{N\}) &= e^c \sum_k e^{-\beta E_k} = 1 ; e^c = \frac{1}{\sum_k e^{-\beta E_k}}
\end{aligned}$$

$$P_k(T, V, \{N\}) = \frac{e^{-\beta E_k}}{\sum e^{-\beta E_k}}$$

$$\text{let } Z(T, V, \{N\}) = \sum_k e^{-\beta E_k}$$

$$\text{therefore } P_k(T, V, \{N\}) = \frac{e^{-\beta E_k}}{Z(T, V, \{N\})}$$

$$Z(T, V, \{N\}) = [z_{\text{trans}}(T)]^N / N!$$

$$Z(T, V, \{N\}) = \left[ \frac{e^{\beta u_0}}{8} \left( \frac{2mk_B T}{\pi \hbar^2} \right)^{\frac{3}{2}} (V - B) \right]^N / N!$$

if  $\tilde{z}_{\text{trans}} = \left( \frac{2mk_B T}{\pi \hbar^2} \right)^{\frac{3}{2}}$  ; then  $Z = \left[ \frac{e^{\beta u_0}}{8} \tilde{z}_{\text{trans}} (V - B) \right]^N / N!$

Sterling Approximation  $Z = \frac{(z_{\text{trans}})^N}{N!} \sim \left( \frac{z_{\text{trans}} e}{N} \right)^N$

$$Z = \left( \frac{\tilde{z}_{\text{trans}} e}{8N} (V - B) e^{\beta u_0} \right)^N$$

$$A(T, V, \{N\}) = -k_B T \ln Z(T, V, \{N\})$$

$$A(T, V, \{N\}) = -k_B T \ln \left( \frac{\tilde{z}_{\text{trans}} e}{8N} (V - B) e^{\beta u_0} \right)^N$$

let  $V \rightarrow V - B$  ;  $u_0 = a \frac{n}{V} \rightarrow a \frac{n}{V - B}$

$$A(T, V, \{N\}) = -k_B T N \ln \left( \frac{\tilde{z}_{\text{trans}} e}{8N} (V - B) e^{\beta \frac{n}{V - B} a} \right)$$

(d)

$$p = -\frac{\partial A}{\partial V}$$

$$= -k_B T N \ln \left( \frac{\tilde{z}_{\text{trans}} e}{8N} \frac{\partial}{\partial V} (V - B) \frac{\partial}{\partial V} e^{\beta \frac{n}{V - B} a} \right)$$

$$\frac{\partial}{\partial V} e^{\beta \frac{n}{V - B} a} = -\beta n a (V - B)^{-2} e^{\beta n a (V - B)^{-1}}$$

$$p = -k_B T N \ln \left[ \left( \frac{\tilde{z}_{\text{trans}} e}{8N} \right) (-\beta n a (V - B)^{-2} e^{\beta n a (V - B)^{-1}}) \right]$$

(e)

$$B \rightarrow (N \times \text{vol})$$

$$B = N_{\text{gas}} \cdot V_{\text{mol}}$$

$$V_{\text{gas}} = N_{\text{gas}} \cdot V_{\text{mol}}$$

$$p = -k_B T N \ln \left[ \left( \frac{\tilde{z}_{\text{trans}} e}{8N} \right) (-\beta n a (V - V_{\text{gas}})^{-2} e^{\beta n a (V - V_{\text{gas}})^{-1}}) \right]$$

1. Problem 2:

(a)

$$p_s + p_f = 1$$

$$n = n_f + n_s$$

$$n_s = n - n_f$$

$$P = p_f^{n_f} \cdot p_s^{n_s}$$

$$P(n, n_f) = \frac{n!}{n_f! n_s!} p_f^{n_f} \cdot p_s^{n_s}$$

$$\binom{n}{n_f} = \frac{n!}{n_f! n_s!} = \frac{n!}{n_f! (n - n_f)!}$$

$$P(n, n_f) = \binom{n}{n_f} (p_f)^{n_f} \cdot (p_s)^{n_s}$$

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In[8]:= Off[General::spell]

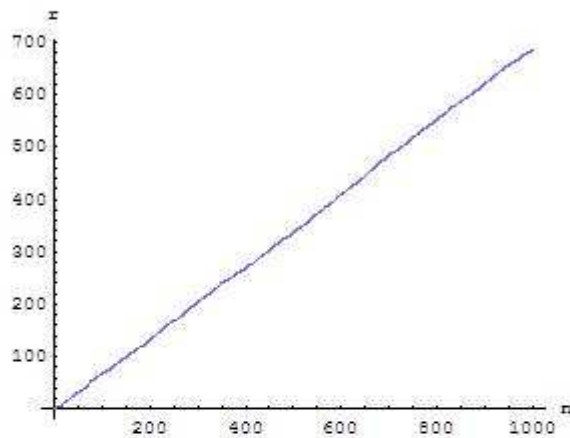
In[9]:= theNo[pf_] := If[Random[] < pf, 1, 0]

In[10]:= randomWalk1Dstay[n_, pf_] := NestList[# + theNo[pf] &, 0, n]

In[11]:= showRandomWalk1Dstay[n_, pf_, opts___] :=
  ListPlot[Transpose[{Range[0, n], randomWalk1Dstay[n, pf]}],
    PlotJoined → True, PlotRange → All,
    PlotStyle → {AbsoluteThickness[0.1],
      RGBColor[0.458, 0.38, 1]}, AxesLabel → {"n", "r"}, opts]

In[12]:= showRandomWalk1Dstay[1000, 0.70, AspectRatio → 0.75]

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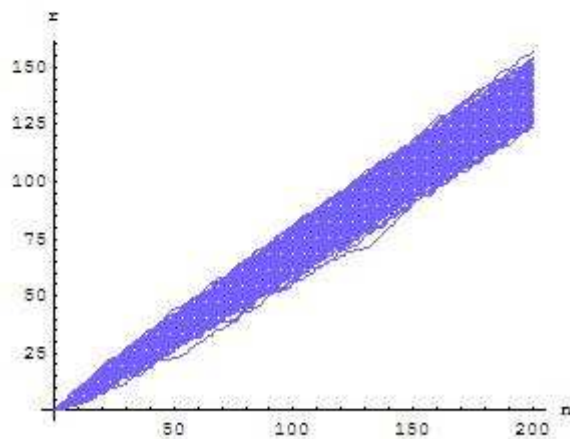
Out[12]= - Graphics -

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In[13]:= rw = Table[showRandomWalk1Dstay[200, 0.7,
  DisplayFunction → Identity], {500}];

In[14]:= Show[rw, DisplayFunction → $DisplayFunction,
  AspectRatio → 0.75]

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Out[14]= - Graphics -

(c) i.

$$\begin{aligned}\text{Let } s &= (n_{f_A} - n_{f_B}) \\ (x_A - x_B) &= s\Delta x \\ (x_A - x_B) &= (n_{f_A} - n_{f_B})\Delta x\end{aligned}$$

ii.

$$\begin{aligned}P(n, s) &= P(B)_0P(A)_s + P(B)_1P(A)_{s+1} + \dots + P(B)_{n-s}P(A)_n + \dots \\ &\dots + P(A)_0P(B)_s + P(A)_1P(B)_{s+1} + \dots + P(A)_{n-s}P(B)_n \\ &= \left( \sum_{n_{f_B}=0}^{n-s} P(B)_{n_{f_B}} P(A)_{n_{f_B}+s} \right) + \left( \sum_{n_{f_A}=0}^{n-s} P(A)_{n_{f_A}} P(B)_{n_{f_A}+s} \right)\end{aligned}$$

The second sum in this equation goes to 0 because  $p_{f_A} > p_{f_B}$  meaning  $n_{f_B} \ll n_{f_A}$ . When there are  $n$  states of the molecule,  $n \rightarrow \infty$  if the walker takes infinite steps, or if the molecular ensemble is very large.

$$P(n, s) = \sum_{n_{f_B}=0}^{n-s} \left[ \frac{n!}{n_{f_B}!n_{s_B}!} (p_{f_B})^{n_{f_B}} \cdot (p_{s_B})^{n_{s_B}} \right] \left[ \frac{n!}{n_{f_B+s}!n_{s_B-s}!} (p_{f_A})^{n_{f_B}+s} \cdot (p_{s_A})^{n_{s_B}-s} \right],$$

where  $n_{s_B} = n - n_{f_B}$ .

iii.

$$P(0 = x_A - x_B) = \sum_{n_f=0}^n \binom{n}{n_f} (p_{f_A})^{n_f} \cdot (p_{s_A})^{n_s} \binom{n}{n_f} (p_{f_B})^{n_f} \cdot (p_{s_B})^{n_s}$$