

Name: \_\_\_\_\_

Answer the questions in the spaces provided. If you run out of room for showing work, continue on the back of the page, but please write your final answer in the box.

All work should be completed on your own, and all students are expected to comply with the BU Academic Code of Conduct.

You will not need a calculator to complete this exam, and you will likely find the equation sheet at the end helpful.

Question	Points	Score
1	25	
2	25	
3	25	
4	25	
Total:	100	

1. (25 points) Robert Brown placed pollen grains of mass,  $m$ , in a cylinder of water at temperature,  $T$ , and measured their heights,  $h$ , above the bottom of the cylinder. The distribution of heights is given by

$$p(h) = C \exp(-mgh/k_B T) \quad (1)$$

where  $g$  is the gravitational acceleration constant,  $k_B$  is Boltzmann's constant, and  $C$  is a normalization constant. The height,  $h$ , varies from 0 to  $\infty$ .

- (a) Determine the value of the normalization constant,  $C$ . It will be a function of  $m$ ,  $g$ ,  $T$ , and  $k_B$ .

**Solution:** Based on the equation sheet,

$$\int_0^{\infty} C \exp(-mgh/k_B T) dh = C \frac{k_B T}{mg} = 1 \implies$$

$$C = \frac{mg}{k_B T}$$

- (b) Determine the average height of the pollen grains  $h$  in terms of  $m$ ,  $g$ ,  $T$ , and  $k_B$ .

**Solution:** For simplicity, let  $\alpha = C = \frac{mg}{k_B T}$ , then

$$\begin{aligned} \langle h \rangle &= \alpha \int_0^{\infty} h e^{-\alpha h} dh \\ &= \alpha \int_0^{\infty} -\frac{d}{d\alpha} e^{-\alpha h} dh \\ &= -\alpha \frac{d}{d\alpha} \int_0^{\infty} e^{-\alpha h} dh \\ &= -\alpha \frac{d}{d\alpha} (\alpha^{-1}) \end{aligned}$$

$$\langle h \rangle = \frac{1}{\alpha} = \frac{k_B T}{mg}$$

- (c) Determine the variance  $\sigma_h^2$  of the distribution function, defined as  $\langle (h - \langle h \rangle)^2 \rangle$ , in terms of  $m$ ,  $g$ ,  $T$ , and  $k_B$ .

**Solution:**

$$\begin{aligned}
 \langle h^2 \rangle &= \alpha \int_0^\infty h^2 e^{-\alpha h} dh \\
 &= \alpha \int_0^\infty \frac{d^2}{d\alpha^2} e^{-\alpha h} dh \\
 &= \alpha \frac{d^2}{d\alpha^2} (\alpha^{-1}) \\
 &= \frac{2}{\alpha^2} \\
 \sigma_h^2 &= \langle h^2 \rangle - \langle h \rangle^2 \\
 &= \frac{2}{\alpha^2} - \left(\frac{1}{\alpha}\right)^2
 \end{aligned}$$

$$\sigma_h^2 = \frac{1}{\alpha^2} = \left(\frac{k_B T}{mg}\right)^2$$

- (d) If the temperature is increased by 10%, what will be the percent change in the average height of the pollen grains?

$$\Delta \langle h \rangle = \frac{\langle h_f \rangle - \langle h_i \rangle}{\langle h_i \rangle} \times 100\% \quad (2)$$

**Solution:**

$$\begin{aligned}
 \Delta \langle h \rangle &= \frac{1.1T \frac{k_B}{mg} - T \frac{k_B}{mg}}{T \frac{k_B}{mg}} \\
 &= 1.1 - 1
 \end{aligned}$$

$$\Delta \langle h \rangle = 10\%$$

2. (25 points) Consider the case of two systems shown below. The energies of the states in each system are labeled.

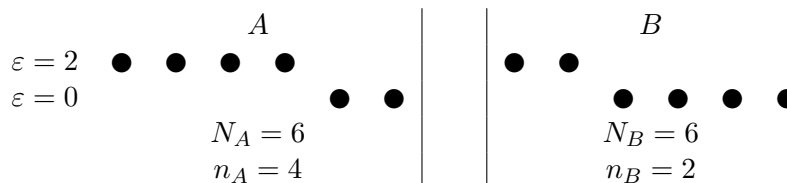


Figure 1: Initial condition for system considered in question 2

- (a) Calculate the energy  $U$  and multiplicity  $W$  for both separate subsystems.

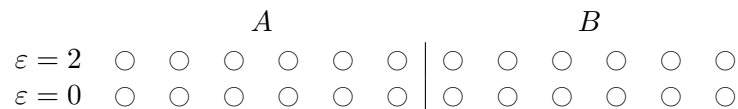
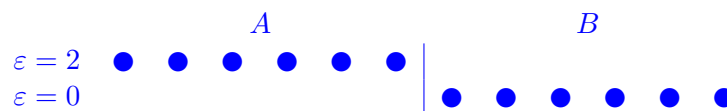
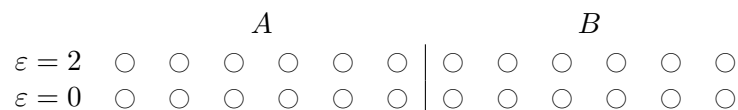
**Solution:**

$$\begin{aligned}
 U_A &= 4 \times 2 = 8 \\
 W_A &= \binom{6}{2} = 15 \\
 U_B &= 2 \times 2 = 4 \\
 W_B &= \binom{6}{4} = 15
 \end{aligned}$$

(b) What are the energy and multiplicity for the total system?

**Solution:**

$$\begin{aligned}
 U_{A+B} &= U_A + U_B = 12 \\
 W_{A+B} &= W_A \times W_B = 225
 \end{aligned}$$

(c) The two systems are brought into thermal contact. Energy can be exchanged between the systems, but the total energy of the combined system is constant. Draw (by filling in the circles) a state of *minimum* multiplicity,  $W_{A+B}$ , that can be achieved.**Solution:**(d) Again following thermal contact, draw a state of *maximum* multiplicity.**Solution:**

(e) Compute the multiplicity of the state drawn in (d). Your answer should be a single number.

**Solution:**

$$W_{\max} = \binom{6}{3}^2 = 400$$

3. (25 points) Consider a diatomic molecule with atoms bound together by a Morse potential:

$$V(r) = D \left( 1 - e^{-\alpha(r-r_e)} \right)^2 \quad (3)$$

where  $D$ ,  $\alpha$ , and  $r_e$  are constants and  $r$  is the distance between the two nuclei.

- (a) What are the point  $r_{\min}$  where the minimum of this function occurs and the value  $V_{\min}$  of the potential at that point?

**Solution:**

$$\begin{aligned}\frac{dV(r_{\min})}{dr} &= 0 = 2\alpha D e^{-\alpha(r-r_e)} \left(1 - e^{-\alpha(r-r_e)}\right) \\ &= e^{-\alpha(r-r_e)} \left(1 - e^{-\alpha(r-r_e)}\right)\end{aligned}$$

$$\boxed{r_{\min} = r_e}$$

$$V_{\min} = V(r_e) = D \left(1 - e^0\right)^2$$

$$\boxed{V_{\min} = 0}$$

- (b) Now, to get an understanding of the behavior near the minimum of the potential, Taylor expand the potential around the minimum point  $r_{\min}$  to second order (up to  $r^2$ , that is).

**Solution:**

Based on the results above, we know that the Taylor series about the point  $r = r_e$  will be 0 for both zeroth and first orders. We then only need to find the second order term:

$$\begin{aligned}V(r) &\approx \frac{1}{2} \left. \frac{d^2V}{dr^2} \right|_{r=r_e} (r - r_e)^2 \\ \frac{d^2V}{dr^2} &= -2\alpha^2 D e^{-\alpha(r-r_e)} \left(1 - 2e^{-\alpha(r-r_e)}\right) \\ \left. \frac{d^2V}{dr^2} \right|_{r=r_e} &= -2\alpha^2 D (1 - 2)\end{aligned}$$

$$\boxed{V(r) \approx \alpha^2 D (r - r_e)^2}$$

- (c) Up to second order we obtain a quadratic expression, which can be thought of as a simple harmonic oscillator potential:

$$V_{\text{SHO}} = \frac{1}{2} k x^2 \tag{4}$$

where  $x$  is the displacement from the potential minimum and  $k$  is the spring constant. From classical physics, we know that the frequency of a harmonic oscillator is  $\omega = \sqrt{\frac{k}{\mu}}$  where  $\mu$  is the reduced mass of the system. Give an expression for the frequency  $\omega$  of this system in terms of  $\mu$ ,  $D$ , and  $\alpha$  assuming the second order Taylor series is sufficiently accurate.

**Solution:**

$$k = 2\alpha^2 D$$

$\therefore$

$$\omega = \alpha \sqrt{\frac{2D}{\mu}}$$

4. (25 points) Consider a one-dimensional lattice. There are  $N/2$  lattice sites on the left of a partition, and  $N/2$  lattice sites on the right. There are  $N/2$  particles, which are indistinguishable from each other, and  $N/2$  empty lattice sites.

- (a) Initially, the system is demixed with  $N/2$  particles on the right side, and  $N/2$  empty sites on the left side. What is the multiplicity of the demixed state?

**Solution:**

$$W_d = 1$$

- (b) Now suppose the particles are free to mix in the total  $N$  sites. What is the multiplicity of the mixed state?

**Solution:**

$$W_m = \binom{N}{N/2} = \frac{N!}{\left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)!}$$

- (c) Using your results from (a) and (b), write an expression for the ratio of the multiplicity of the demixed state and the mixed state.

**Solution:**

$$\frac{W_d}{W_m} = \frac{\left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)!}{N!}$$

- (d) Assuming  $N \gg 1$ , use Stirling's approximation to simplify the result in (c).

**Solution:**

$$\frac{W_d}{W_m} = \frac{\left(\frac{N}{2e}\right)^{2N/2}}{\left(\frac{N}{e}\right)^N} = 2^{-N}$$

- (e) Using your result from (d), determine the limit of the ratio as  $N \rightarrow \infty$ .

**Solution:**

$$\lim_{N \rightarrow \infty} \frac{W_d}{W_m} = 0$$

The probability of being unmixed goes to 0 as the system size increases.

Table 1: Fundamental and derived constants

Name	Symbol	Value	Units
Atomic Mass Unit	$u$	$1.660\,54 \times 10^{-27}$	kg
Avogadro's Number	$N_A$	$6.022\,14 \times 10^{23}$	$\text{mol}^{-1}$
Mass of an Electron	$m_e$	$9.109\,38 \times 10^{-31}$	kg
Mass of a Neutron	$m_n$	$1.674\,93 \times 10^{-27}$	kg
Mass of a Proton	$m_p$	$1.672\,62 \times 10^{-27}$	kg
Faraday's Constant	$F$	$9.648\,53 \times 10^4$	C/mol
Gas Constant	$R$	8.314 46	J/(K mol)
		0.082 06	L atm/(K mol)
		62.363 58	L Torr/(K mol)
Boltzmann's Constant	$k_B$	$1.380\,65 \times 10^{-23}$	J/K
Planck's Constant	$h$	$6.626\,07 \times 10^{-34}$	J s
Speed of Light	$c$	$2.997\,92 \times 10^8$	m/s
Earth's Gravitational Constant	$g$	9.806 65	$\text{m/s}^2$
Bohr Radius	$a_0$	$5.291\,77 \times 10^{-11}$	m
Rydberg Constant	$R_\infty$	$1.097\,37 \times 10^7$	$\text{m}^{-1}$
Hartree Energy	$E_h$	$4.359\,74 \times 10^{-18}$	J

Table 2: Formulas

$\ln 2 = 0.693$	$c_V = \frac{3}{2}R$	$\Delta S_{\text{sys}} = nc_P \ln \left( \frac{T_2}{T_1} \right)$
$\ln 3 = 1.099$	$\Delta U = nc_V \Delta T$	$\Delta S_{\text{sys}} = nc_V \ln \left( \frac{T_2}{T_1} \right)$
$\ln 5 = 1.609$	$\Delta H = nc_P \Delta T$	$\int_0^\infty e^{-\alpha x} dx = \frac{1}{\alpha}$
$\ln N! \approx N \ln N - N$	$w = - \int_{V_1}^{V_2} P_{\text{ext}}(V) dV$	$\int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$
$\Delta U = q + w$	$w = -nRT \ln \left( \frac{V_2}{V_1} \right)$	$\int_0^\infty x e^{-\alpha x^2} dx = \frac{1}{2\alpha}$
$H = U + PV$	$w = -P_{\text{ext}} \Delta V$	$\int_0^\infty x^2 e^{-\alpha x^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{\alpha^3}}$
$q = mc_s \Delta T$	$\Delta S_{\text{sys}} = \int_1^2 \frac{dq_{\text{rev}}}{T}$	$N! \approx \left( \frac{N}{e} \right)^N$
$q_{\text{calorimeter}} = C_{\text{calorimeter}} \Delta T$	$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$	
$c_P = c_v + R$	$\Delta S_{\text{sys}} = nR \ln \left( \frac{V_2}{V_1} \right)$	
$c_P = \frac{5}{2}R$	$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}}$	$f(x) = \sum_{i=0}^{\infty} \frac{1}{i!} \left. \frac{d^i f(x)}{dx^i} \right _{x=a} (x-a)^i$