NAME and ID NUMBER:

There should be 8 pages to this exam, counting this cover sheet. Please check this exam NOW!

There are 5 pages of formulae/data, and a periodic table (with molar masses) at the back of this exam. Books, notes, etc. are not permitted, however calculators are. Partial credit will be given but only if your answers can be deciphered. Therefore, make sure that your writing is neat and that your logic is clear, organized, and easy to follow. Unreadable answers will not be given the benefit of the doubt. Choose any 3 of the four questions, and supply your answers in the examination booklets provided. Solve all 4 problems for extra credit, but be sure to indicate clearly which one you wish to have considered as your extra credit problem. Good luck.

GRADING

1. (33 points)

2. (33 points)

3. (33 points)

4. (33 points)

TOTAL: 99 points

Extra Credit (33 possible points):
1. (33 points)
   The van der Waals equation of state is
   \[ P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \]
   and the energy of a van der Waals gas or liquid is
   \[ E = \frac{3}{2} nRT - \frac{an^2}{V} \]
   Up to irrelevant additive constants, what is its Helmholtz free energy function \( A(n,V,T) \), assuming that the particles are indistinguishable?

2. (33 points)
   Near the liquid-gas critical point, it is observed experimentally that the equation of state behaves as
   \[ P - P_c \sim (\rho - \rho_c)^\delta \]
   where \( \delta \) is another example of a critical exponent. Here \( \rho_c = n/V_c \) is the critical density, \( V_c \) is the critical volume, and \( P_c \) is the critical pressure. This behavior is observed when \( T = T_c \), where \( T_c \) is the critical temperature. In this problem, you will use the van der Waals equation to predict a value for the exponent \( \delta \). Recall that in terms of density, the van der Waals equation is
   \[ P = \frac{\rho RT}{1 - \rho b} - a\rho^2 \]
   Given this, the value of \( \delta \) can be obtained by performing a Taylor expansion of this equation about \( \rho = \rho_c = (1/3b) \) when \( T = T_c = 8a/27Rb \). This expansion takes the form
   \[ P - P_c = \sum_{k=1}^{\infty} \frac{1}{k!} \frac{\partial^k P}{\partial \rho^k} \bigg|_{\rho=\rho_c, T=T_c} (\rho - \rho_c)^k \]
   and the first nonzero term in the expansion gives the value of \( \delta \). Using this procedure, what value for \( \delta \) does the van der Waals equation yield?

3. (33 points)
   Consider two thermodynamic states of a system, denoted \( \mathcal{A} \) and \( \mathcal{B} \), characterized by energy levels \( E_j^{(A)}(N,V) \) and \( E_j^{(B)}(N,V) \). One way to drive the system from state \( \mathcal{A} \) to \( \mathcal{B} \) is to do so continuously by introducing a parameter \( \lambda \in [0,1] \) and a set of energy levels
   \[ E_j(\lambda,N,V) = f(\lambda)E_j^{(A)}(N,V) + g(\lambda)E_j^{(B)}(N,V) \]
   where \( f(\lambda) \) and \( g(\lambda) \) are two arbitrary functions.
   a. (4 points)
      As \( \lambda \) is continuously varied from 0 to 1, the system continuously transforms from state \( \mathcal{A} \), with energy levels \( E_j^{(A)}(N,V) \) at \( \lambda = 0 \), to \( \mathcal{B} \), with energy levels \( E_j^{(B)}(N,V) \) at \( \lambda = 1 \). Given this requirement, what conditions must the functions \( f(\lambda) \) and \( g(\lambda) \) satisfy at the endpoints, \( \lambda = 0 \) and \( \lambda = 1 \)?
   b. (6 points)
      Write down one possible choice for \( f(\lambda) \) and \( g(\lambda) \) that obey the restrictions you obtained in part a.
   c. (15 points)
      Define a \( \lambda \)-dependent partition function
      \[ Q(N,V,T,\lambda) = \sum_j e^{-\beta E_j(\lambda,N,V)} \]
and a $\lambda$-dependent Helmholtz free energy

$$A(N, V, T, \lambda) = -k_B T \ln Q(N, V, T, \lambda)$$

Show that the free energy difference between states $A$ and $B$ can be computed from

$$\Delta A_{AB} = \int_0^1 \left\langle \frac{\partial E}{\partial \lambda} \right\rangle_\lambda d\lambda$$

where

$$\left\langle \frac{\partial E}{\partial \lambda} \right\rangle_\lambda \equiv \frac{1}{Q(N, V, T, \lambda)} \sum_j \left( \frac{\partial E_j(N, V, \lambda)}{\partial \lambda} \right) e^{-\beta E_j(N, V, \lambda)}$$

**Hint:** Try starting from the trivial relation from the fundamental theorem of calculus:

$$\Delta A_{AB} = \int_0^1 \frac{\partial A}{\partial \lambda} d\lambda$$

d. (8 points)

Now consider an ideal gas of $N$ particles at temperature $T$. Let $n_1, ..., n_N$ denote the $N$ quantum numbers. Suppose the system undergoes an expansion from a volume $V_A$ to volume $V_B$ at fixed $T$. Using the functions $f(\lambda)$ and $g(\lambda)$ you devised in part b, write down the corresponding expression for the $\lambda$-dependent energy levels $E_{n_1, ..., n_N}(N, V, \lambda)$ you would use to carry out the procedure in part c.

4. (33 points)

A monatomic ideal gas is taken around the following thermodynamic cycle:

i. An isothermal expansion from volume $V_A$ to volume $V_B$ at temperature $T_h$.

ii. An isochoric cooling from temperature $T_h$ to temperature $T_i$.

iii. An isothermal compression from volume $V_B$ to volume $V_A$ at temperature $T_i$.

iv. An isochoric warming from temperature $T_i$ to temperature $T_h$, which returns the system to its initial state.

a. (11 points)

Sketch the cycle in both the $P-V$ and $T-S$ planes, and give the equations that determine curves for each segment of the cycle in both the $P-V$ and $T-S$ planes.

b. (5 points)

Calculate the energy and entropy change in each step of the cycle, and show that the net change in energy and the net change in entropy around the cycle are both zero.

c. (17 points)

The partition function for a monatomic ideal gas is

$$Q(N, V, T) = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N$$

where $\lambda = \sqrt{\hbar^2/2\pi m}$. Calculate the Helmholtz free energy change for each step of the cycle, show that the net change in the Helmholtz free energy is zero around the cycle, and find the net work output of the cycle.
POSSIBLY USEFUL INFORMATION

\[ N_0 = 6.022 \times 10^{23} \text{ mol}^{-1} \]

\[ R = 8.31441 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 0.082057 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \]

\[ k_B = 1.38066 \times 10^{-23} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.36262 \times 10^{-25} \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \]

\[ h = 6.62609 \times 10^{-34} \text{ J} \cdot \text{s}, \quad \hbar = \frac{h}{2\pi} = 1.05457 \times 10^{-34} \text{ J} \cdot \text{s} \]

Some conversion factors

- \( 1 \, \text{Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} \)
- \( 1 \, \text{L} = 10^{-3} \text{ m}^3 = 10^3 \text{ cm}^3 \)
- \( 1 \, \text{J} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \)
- \( 1 \, \text{atm} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mm Hg at } 0^\circ\text{C} = 760 \text{ torr} \)
- \( 1 \, \text{Pa} = 1 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2} \)
- \( 1 \, \text{L} \cdot \text{atm} = 101.325 \text{ J} \)

Formulas

\[ PV = nRT, \quad \gamma = \frac{c_p}{c_V}, \quad c_p = c_V + R, \quad E = \frac{3}{2} nRT = \frac{3}{2} N k_B T \]

\[ \Omega(N, V, E) = \frac{1}{N!} \left( \frac{mE}{3N\pi R^2} \right)^{3N/2} V^N, \quad n = \frac{N}{N_0}, \quad R = N_0 k_B \]

\[ S(N, V, E) = k_B \ln \Omega(N, V, E), \quad \Delta S_{AB} = \int_A^B \frac{dQ_{rev}}{T} = k_B \ln \left( \frac{\Omega_B}{\Omega_A} \right) \]

\[ E = Q + W \]
\[ A = E - TS = \mu N - PV, \quad G = A + PV = \mu N - TS \]

At a critical point: \[ \frac{\partial P}{\partial V} = 0, \quad \frac{\partial^2 P}{\partial V^2} = 0 \]

\[ Q(N, V, T) = \sum_j e^{-\beta E_j(N, V)} \]

\[ E = -\frac{\partial}{\partial \beta} \ln Q(N, V, T), \quad P = -k_B T \left( \frac{\partial \ln Q(N, V, T)}{\partial V} \right), \]

\[ A(N, V, T) = -k_B T \ln Q(N, V, T), \quad P = -\left( \frac{\partial A}{\partial V} \right)_{N,T} \]

\[ S = -\left( \frac{\partial A}{\partial T} \right)_{N,V} = k_B \ln Q + \frac{E}{T} \]

\[ \Delta A = W_{\text{rev}} \quad \text{(isothermal)} \]

\[ \Delta(N, P, T) = \int_0^\infty e^{-\beta PV} Q(N, V, T) dV \]

\[ H = -\frac{\partial}{\partial \beta} \ln \Delta(N, P, T), \quad \langle V \rangle = -k_B T \left( \frac{\partial \ln \Delta(N, P, T)}{\partial P} \right), \]

\[ G(N, P, T) = -k_B T \ln \Delta(N, P, T), \quad \langle V \rangle = \left( \frac{\partial G}{\partial P} \right)_{N,T} \]

\[ S = -\left( \frac{\partial G}{\partial T} \right)_{N,P} = k_B \ln \Delta + \frac{H}{T} \]

\[ \hat{H}_\psi = E\psi, \quad E \neq mc^2 \]

\[ E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2, \quad E_n = \frac{\hbar^2 \pi^2}{2mV^{2/3}} |n|^2 \]

\[ E_n = \left( n + \frac{1}{2} \right) \hbar \omega, \quad E_n = \left( n_x + n_y + n_z + \frac{3}{2} \right) \hbar \omega \]

\[ E_{JM} = \frac{\hbar^2}{2I} J(J + 1) \]

\[ F_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2} \]
Mathematics

Vectors:

\[ \mathbf{a} = (a_x, a_y, a_z) \]

\[ |\mathbf{a}| = \sqrt{a_x^2 + a_y^2 + a_z^2} \]

\[ \mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z \]

\[ \mathbf{a} + \mathbf{b} = (a_x + b_x, a_y + b_y, a_z + b_z) \]

\[ |\mathbf{a} + \mathbf{b}| = \sqrt{|\mathbf{a}|^2 + |\mathbf{b}|^2 + 2 \mathbf{a} \cdot \mathbf{b}} \]

\[ \theta = \cos^{-1}\left[ \frac{\mathbf{a} \cdot \mathbf{b}}{|\mathbf{a}| |\mathbf{b}|} \right] \]

Identities

\[ \ln x + \ln y = \ln(xy), \quad \ln x - \ln y = \ln\left(\frac{x}{y}\right) \]

\[ e^{x+y} = e^x e^y, \quad \frac{1}{e^x} = e^{-x} \]

Sums and integrals:

\[ \sum_{n=0}^{\infty} r^n = \frac{1}{1 - r}, \quad 0 < r < 1 \]

\[ \sum_{n,m} a_m b_n = \left( \sum_{m} a_m \right) \left( \sum_{n} b_n \right) \]

\[ f(x) = \sum_{k=0}^{\infty} \frac{1}{k!} f^{(k)}(x_0)(x - x_0)^k, \quad \text{(Taylor series expansion about } x = x_0) \]

\[ \int \frac{dx}{x} = \ln x + C, \quad \int x^n dx = \frac{x^{n+1}}{n+1} + C \]

Fundamental Theorem of Calculus:

\[ \int_{a}^{b} f(x) dx = F(b) - F(a) \]

\[ \frac{dF}{dx} = f(x) \]
Euler’s Theorem:

If \( f(\lambda x_1, ..., \lambda x_k, x_{k+1}, ..., x_M) = \lambda^n f(x_1, ..., x_M) \)

Then \( nf(x_1, ..., x_M) = \sum_{i=1}^{k} x_i \frac{\partial f}{\partial x_i} \)

Legendre transform: Given \( f(x) \) and \( y = f'(x) = g(x) \),

\[ b(y) = f(x(y)) - x(y)f'(x(y)) \]
FIG. 1: Periodic table.

* Lanthanide series

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** Actinide series

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