

Physics 7602 Midterm Exam (Part 1 of 2) – Spring 2020

- Closed-book exam: no notes, no phone
- Please begin each of the 3 problems on a new page of your exam book.

Problem 1. (35 pts)

The Gibbs free energy $G = U - TS + PV$ is the most natural thermodynamic potential for a system held at constant temperature and constant pressure. The thermodynamic relation for G is $dG = -S dT + V dP + \mu dN$.

- 5 A. Determine the thermodynamic relation for G starting from the thermodynamic relation for U .

$$dU = T dS - P dV + \mu dN$$

$$dG = dU - d(TS) + d(PV) = (T dS - P dV + \mu dN) - (T dS + S dT) + (P dV + V dP)$$

$$= -S dT + V dP + \mu dN$$

The conditions that G and N are extensive while T and P are intensive imply that $G(T, P, \lambda N) = \lambda G(T, P, N)$.

- 5 B. Use this to deduce that $G = N\mu$, where μ is the chemical potential.

differentiate w.r.t. λ : $\frac{\partial}{\partial(\lambda N)} G(T, P, \lambda N) \cdot \frac{d}{d\lambda} (\lambda N) = \left(\frac{d}{d\lambda} \lambda\right) G(T, P, N)$

set $\lambda = 1$: $\frac{\partial}{\partial N} G(T, P, N) \cdot N = G(T, P, N)$

identify derivative: $\left(\frac{\partial G}{\partial N}\right)_{T, P} = \mu \implies G = N\mu$

The differential of G can be expressed as $dG = N d\mu + \mu dN$.

- 5 C. Use this together with the thermodynamic relation for G to deduce a relation between the differentials of μ , T , and P that involves only intensive quantities.

$$N d\mu + \mu dN = -S dT + V dP + \mu dN$$

$$N d\mu = -S dT + V dP$$

divide by N : $d\mu = -\frac{S}{N} dT + \frac{V}{N} dP$

A phase transition line in the temperature-pressure plane separates two phases A and B . Along this line, the two phases can coexist with pressure $P_{AB}(T)$ as a function of T . The condition for chemical equilibrium between the two phases can be expressed as

$$\mu_A(P_{AB}(T), T) = \mu_B(P_{AB}(T), T).$$

- 5 D. Derive an expression for the slope dP_{AB}/dT of the phase transition line. (The results of part C could be used to express the slope in terms of the specific entropy and the specific volume, but this is not necessary.)

differentiate w.r.t. t : $\left(\frac{\partial \mu_A}{\partial P}\right)_T \frac{d}{dT} P_{AB}(T) + \left(\frac{\partial \mu_A}{\partial T}\right)_P = \left(\frac{\partial \mu_B}{\partial P}\right)_T \frac{d}{dT} P_{AB}(T) + \left(\frac{\partial \mu_B}{\partial T}\right)_P$

solve for $\frac{dP_{AB}}{dT}$: $\frac{dP_{AB}}{dT} = \frac{\left(\frac{\partial \mu_B}{\partial T}\right)_P - \left(\frac{\partial \mu_A}{\partial T}\right)_P}{\left(\frac{\partial \mu_A}{\partial P}\right)_T - \left(\frac{\partial \mu_B}{\partial P}\right)_T}$

A system at fixed temperature and pressure consists of three types of particles: A, B, and C. The Gibbs free energy can be expressed as

$$G = N_A \mu_A + N_B \mu_B + N_C \mu_C.$$

The three particles can undergo the chemical reaction $nA + mB \leftrightarrow pC$, where n , m , and p are integers.

5 E. What is the change ΔG in the Gibbs free energy from a single forward reaction?

$$\begin{aligned} \Delta N_A &= -n & \Delta N_B &= -m & \Delta N_C &= +p \\ \Delta G &= \mu_A \Delta N_A + \mu_B \Delta N_B + \mu_C \Delta N_C \\ &= -n\mu_A - m\mu_B + p\mu_C \end{aligned}$$

If a system that is not in equilibrium is held at constant temperature and constant pressure, the Gibbs free energy will decrease. When the system reaches equilibrium, the Gibbs free energy will have its minimum possible value.

5 F. Use the minimization of the Gibbs free energy to deduce a relation between the chemical potentials μ_A , μ_B , and μ_C at equilibrium.

$$\begin{aligned} \text{minimize } G \text{ w.r.t. number of reactions} &\implies dG = 0 \\ dN \text{ reactions} &\implies dN_A = -m dN, \quad dN_B = -n dN, \quad dN_C = +p dN \\ dG = \mu_A dN_A + \mu_B dN_B + \mu_C dN_C &= (-m\mu_A - n\mu_B + p\mu_C) dN \quad dG = 0 \\ &\implies m\mu_A + n\mu_B = p\mu_C \end{aligned}$$

A gas consisting of the atoms A and B and the diatomic molecule AB is in thermal equilibrium at temperature T . The chemical potential for the atom A is

$$\mu_A = -kT \log \frac{(m_A kT / 2\pi \hbar^2)^{3/2}}{n_A},$$

where n_A is the number density of A. The chemical potentials for B and AB have similar expressions but with masses m_B and $m_A + m_B$ and with number densities n_B and n_{AB} .

~~X~~ In equilibrium, the following combination of number densities must be equal to an equilibrium constant $K(T)$:

$$\frac{n_{AB}}{n_A n_B} = K(T).$$

5 G. Deduce $K(T)$ from the condition for chemical equilibrium with respect to the reaction $A + B \leftrightarrow AB$.

(If $\log x + \log y = \log z$, then $xy = z$.)

$$\begin{aligned} \text{chemical equilibrium} &\implies \mu_A + \mu_B = \mu_{AB} \\ -kT \log \frac{(m_A kT / 2\pi \hbar^2)^{3/2}}{n_A} - kT \log \frac{(m_B kT / 2\pi \hbar^2)^{3/2}}{n_B} &= -kT \log \frac{((m_A + m_B) kT / 2\pi \hbar^2)^{3/2}}{n_{AB}} \\ \frac{(m_A kT / 2\pi \hbar^2)^{3/2}}{n_A} \cdot \frac{(m_B kT / 2\pi \hbar^2)^{3/2}}{n_B} &= \frac{((m_A + m_B) kT / 2\pi \hbar^2)^{3/2}}{n_{AB}} \\ \frac{n_{AB}}{n_A n_B} &= \left(\frac{m_A + m_B}{m_A m_B} \frac{2\pi \hbar^2}{kT} \right)^{3/2} \implies K(T) = \left(\frac{m_A + m_B}{m_A m_B} \frac{2\pi \hbar^2}{kT} \right)^{3/2} \end{aligned}$$

Problem 2. (32 points)

Three ensembles often used in statistical mechanics are

- MCE: microcanonical ensemble,
- CE: canonical ensemble,
- GCE: grand canonical ensemble.

Consider the following three systems of gases:

- I. an isolated system consisting of N molecules in a volume V ,
- II. a system consisting of N molecules in a volume V in thermal contact with a much larger reservoir,
- III. a system consisting of those molecules that are instantaneously within a region of volume V inside a much larger volume containing a gas of the molecules.
(The system of volume V is not separated from the reservoir by any walls.)

For each of the three systems I, II, and III, list the appropriate ensembles (MCE and/or CE and/or GCE or none of the above). The answers are already given for system I.

3 A. List the ensembles that can accurately determine the equation of state relating P , V/N , and T in the thermodynamic limit.

- I: MCE, CE, GCE
 - II: MCE, CE, GCE
 - II: MCE, CE, GCE
- } all 3 give same thermodynamic limit

3 B. List the ensembles that can accurately determine the average energy U as a function of N , T , and V/N in the thermodynamic limit.

- I: MCE, CE, GCE
 - II: MCE, CE, GCE
 - II: MCE, CE, GCE
- } all 3 give same thermodynamic limit

3 C. List the ensembles that give a reasonable approximation to the fluctuations in the energy of the system.

- I: MCE — no fluctuations in energy
- II: CE
- II: GCE

3 D. List the ensembles that give a reasonable approximation to the fluctuations in the number of particles in the system.

- I: MCE, CE
 - II: MCE, CE
 - II: GCE
- } both give no fluctuations in N

An ensemble can be defined by specifying the probability P_r for every microstate r .
 The average energy $U = \langle E \rangle$ can be expressed as a sum over microstates: $U = \sum_r P_r E_r$.

Given the average energy U , the root-mean-square deviation ΔE for fluctuations in the energy is defined by $(\Delta E)^2 = \langle (E - U)^2 \rangle$.

4 E. Express $(\Delta E)^2$ as a sum over microstates.

$$(\Delta E)^2 = \sum_r P_r (E_r - U)^2$$

4 F. Show that ΔE can be determined from the two averages $\langle E^2 \rangle$ and $U = \langle E \rangle$.

$$\begin{aligned} (\Delta E)^2 &= \langle (E - U)^2 \rangle = \langle E^2 - 2EU + U^2 \rangle \\ &= \langle E^2 \rangle - 2U \langle E \rangle + U^2 = \langle E^2 \rangle - 2U \cdot U + U^2 \\ &= \langle E^2 \rangle - U^2 = \langle E^2 \rangle - \langle E \rangle^2 \end{aligned}$$

The partition function for the canonical ensemble is $Z = \sum_r e^{-\beta E_r}$.

4 G. Express the average energy U in terms of a derivative of Z .

$$\begin{aligned} U &= \frac{1}{Z} \sum_r P_r e^{-\beta E_r} = \frac{1}{Z} \sum_r \left(-\frac{\partial}{\partial \beta} \right) e^{-\beta E_r} \\ &= \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \right) \sum_r e^{-\beta E_r} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z \end{aligned}$$

The mean-square deviation for fluctuations in the energy can be expressed as $(\Delta E)^2 = -(\partial U / \partial \beta)_{V,N}$.

4 H. Deduce how ΔE scales with the number N of particles in the thermodynamic limit.

$$U \text{ scales as } N^1, \quad \beta = \frac{1}{T} \text{ scales as } N^0$$

$$\implies (\Delta E)^2 \text{ scales as } \frac{N^1}{N^0} = N$$

$$\implies \Delta E \text{ scales as } \sqrt{N}$$

4 I. Express ΔE in terms of an appropriate heat capacity: $C_X = (T \partial S / \partial T)_X$.

$$dU = T ds - P dV + \mu dN \implies \left(\frac{\partial U}{\partial T} \right)_{V,N} = T \left(\frac{\partial S}{\partial T} \right)_{V,N}$$

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{V,N} = \left(\frac{\partial U}{\partial T} \right)_{V,N}$$

$$(\Delta E)^2 = - \left(\frac{\partial U}{\partial \beta} \right)_{V,N} = + T^2 \left(\frac{\partial U}{\partial T} \right)_{V,N} = T^2 C_V$$

Problem 3.

The partition function for a gas of N atoms (or molecules) at temperature $T = 1/\beta$ in a volume V is

$$Z_N = \frac{1}{N!} \left(\frac{V}{(2\pi\hbar^2/mkT)^{3/2}} Z_{\text{int}} \right)^N$$

where Z_{int} is the internal partition function.

A. Express the factor depending on V and T as an explicit integral over the coordinates and momenta of an atom.

$$\frac{V}{(2\pi\hbar^2/mkT)^{3/2}} = \frac{1}{(2\pi\hbar)^3} \underbrace{\int d^3r}_{\text{volume } V} \underbrace{\int d^3p}_{\text{all momenta}} e^{-\beta p^2/2m}$$

The Helmholtz free energy F can be expressed as the sum of the free energy F_{ideal} of an ideal gas and the internal free energy F_{int} .

B. Determine F_{gas} and F_{int} in the thermodynamic limit.

($\log N! \approx N \log N - N$.) (F_{ideal})

$$F = -\frac{1}{\beta} \log Z_N = -kT \left[\log \frac{V}{(2\pi\hbar^2/mkT)^{3/2}} + \log Z_{\text{int}} - \underbrace{\log(N!)}_{\approx N \log N - N} \right]$$

$$F_{\text{ideal}} = -NkT \left[\log \frac{V}{(2\pi\hbar^2/mkT)^{3/2}} - \log N + 1 \right]$$

$$F_{\text{int}} = -NkT \log Z_{\text{int}}$$

In a gas of atoms at ordinary temperature, Z_{int} just counts the number of quantum spin states.

C. Determine Z_{int} for

• a hydrogen atom H
(spin $-\frac{1}{2}$ electron bound to a spin $-\frac{1}{2}$ proton), $Z_{\text{int}} = 2 \times 2 = 4$

• a deuterium atom D
(spin $-\frac{1}{2}$ electron bound to a spin -1 deuteron). $Z_{\text{int}} = 2 \times 3 = 6$

D. What is the internal entropy S_{int} for an H atom? $S_{\text{int}} = \log 4$

$dF = -SdT + PdV + \mu dN$ for a D atom? $S_{\text{int}} = \log 6$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \Rightarrow \frac{S_{\text{int}}}{N} = -\frac{1}{N} \frac{dF_{\text{int}}}{dT} = k \log Z_{\text{int}}$$

For a gas of diatomic molecules that consist of two different atoms, the internal partition function is the product of vibrational, rotational, and nuclear-spin terms.

$$Z_{\text{int}} = Z_{\text{vib}} Z_{\text{rot}} Z_{\text{nuc}}$$

At ordinary temperatures, the nuclear-spin term Z_{nuc} simply counts the number of spin states of the two nuclei.

E. What is Z_{nuc} for the hydrogen-deuterium molecule HD ? $Z_{\text{nuc}} = 2 \times 3 = 6$

for the hydrogen diatomic molecule H_2 ? $Z_{\text{nuc}} = 2 \times 2 = 4$

The vibrational Hamiltonian for the HD molecule can be approximated by

$$H_{\text{vib}} = \frac{1}{2\mu} \frac{p^2}{r^2} + \varepsilon_0 + \frac{1}{2} \mu \omega^2 (r - r_0)^2,$$

where r_0 is the equilibrium radius that minimizes the interatomic potential $V(r)$, $\varepsilon_0 = V(r_0)$, $\mu \omega^2 = V''(r_0)$, and μ is the reduced mass of the two atoms.

F. Express the vibrational partition function Z_{vib} as an explicit sum over vibrational quantum numbers.

quantum harmonic oscillator: $\varepsilon_n = \varepsilon_0 + (n + \frac{1}{2}) \hbar \omega$ $n=0,1,2,\dots$

$$Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta \varepsilon_n} = e^{-\beta(\varepsilon_0 + \frac{1}{2} \hbar \omega)} \sum_{n=0}^{\infty} e^{-\beta n \hbar \omega}$$

G. Use the equipartition theorem to deduce the high-temperature limit of the vibrational energy $\langle \varepsilon_{\text{vib}} \rangle$ of a single molecule.

equipartition: average of quadratic term in H is $\frac{1}{2} kT$

$$\langle \varepsilon_{\text{vib}} \rangle = \langle H_{\text{vib}} \rangle = \left\langle \frac{1}{2} \mu p^2 \right\rangle + \varepsilon_0 + \left\langle \frac{1}{2} \mu \omega^2 (r - r_0)^2 \right\rangle = \varepsilon_0 + 2 \cdot \frac{1}{2} kT$$

H. Estimate the temperature scale below which vibrations freeze out due to quantum effects.

$$kT \lesssim \hbar \omega \quad (\text{only energy scale in sum over } n \text{ in } Z_{\text{vib}})$$

The rotational partition function can be expressed as a sum over orbital-angular-momentum quantum numbers:

$$Z_{\text{rot}} = \sum_{\ell=0}^{\infty} (2\ell + 1) e^{-\beta \ell(\ell+1) \hbar^2 / 2I},$$

where $I = \mu r_0^2$ is the moment of inertia of the molecule.

I. Derive the high-temperature limit of Z_{rot} by approximating the sum over ℓ by an integral.

$$\begin{aligned} Z_{\text{rot}} &\approx \int_0^{\infty} d\ell (2\ell + 1) e^{-\beta \ell(\ell+1) \hbar^2 / 2I} = \int_0^{\infty} d(\ell(\ell+1)) e^{-\beta \ell(\ell+1) \hbar^2 / 2I} \\ &= \int_0^{\infty} dx e^{-(\beta \hbar^2 / 2I) x} = \frac{2I}{\beta \hbar^2} = \frac{2I}{\hbar^2} kT \end{aligned}$$

J. Estimate the temperature scale below which rotations freeze out due to quantum effects.

$$kT \lesssim \frac{\hbar^2}{2I} \quad (\text{only energy scale in } Z_{\text{rot}})$$

For a diatomic molecule consisting of identical atoms, it is necessary to take into account the indistinguishability of the two nuclei.

K. Determine the partition function $Z_{\text{rot}/\text{nuc}}$ for rotations and nuclear spins for the hydrogen diatomic molecule H_2 .

(The nucleus of H is a spin- $\frac{1}{2}$ proton. The total nuclear spin for H_2 can be in a symmetric triplet state or an antisymmetric singlet state.)

proton is fermion \Rightarrow wavefunction must be odd under interchange of protons
 nuclear spin state: triplet (3 states, symmetric) or singlet (1 state, antisymmetric)
 rotational state changes by $(-1)^\ell$: symmetric if ℓ even, antisymmetric if ℓ odd

$$Z_{\text{rot}/\text{nuc}} = 3 \sum_{\substack{\ell=0 \\ \ell \text{ odd}}}^{\infty} e^{-\beta \varepsilon_\ell} + 1 \cdot \sum_{\substack{\ell=0 \\ \ell \text{ even}}}^{\infty} e^{-\beta \varepsilon_\ell}, \quad \varepsilon_\ell = \ell(\ell+1) \hbar^2 / 2I$$