

**University of Illinois at Chicago
Department of Physics**

SOLUTIONS

***Thermodynamics and Statistical Mechanics
Qualifying Examination***

**January 7, 2011
9:00 AM to 12:00 Noon**

Full credit can be achieved from completely correct answers to 4 questions. If the student attempts all 5 questions, all the answers will be graded, and the top 4 scores will be counted towards the exam's total score.

Equation Sheet

$$\int_{-\infty}^{\infty} \exp[-bx^2] dx = \sqrt{\frac{\pi}{b}}$$

$$\int_0^{\infty} x^2 \exp[-bx^2] dx = \frac{1}{4} \sqrt{\frac{\pi}{b^3}}$$

$$\int_0^{\infty} x^2 \exp[-x] dx = 2$$

$$\int_0^{\infty} dx \frac{x}{e^x - 1} = \frac{\pi^2}{6}$$

$$\int_0^{\infty} dx \frac{x}{e^x + 1} = \frac{\pi^2}{12}$$

$$\int_0^{\infty} dx \frac{x^2}{e^x - 1} = 2 \zeta(3), \text{ where } \zeta(3) \text{ can be considered to be just a number.}$$

$$\int_0^{\infty} dx \frac{x^2}{e^x + 1} = \frac{3}{2} \zeta(3)$$

$$\bar{n} = \frac{1}{e^{(\epsilon - \mu)/kT} \pm 1}$$

$$\sinh(x) = \frac{1}{2}(e^x - e^{-x})$$

$$\cosh(x) = \frac{1}{2}(e^x + e^{-x})$$

$$\frac{d}{dx} [\sinh(x)] = \cosh(x)$$

$$\frac{d}{dx} [\cosh(x)] = \sinh(x)$$

$$\sum_{m=0}^{\infty} x^m = \frac{1}{1-x}$$

$$\sum_{m=0}^n x^m = \frac{1-x^{n+1}}{1-x}$$

Problem 1

A gas of N identical classical non-interacting atoms is held in a potential $V(r) = ar$, where $r = (x^2 + y^2 + z^2)^{1/2}$. The gas is in thermal equilibrium at temperature T .

- (a) Find the single particle partition function Z_1 of an atom in the gas. Express your answer in the form $Z_1 = AT^\alpha a^{-\eta}$ and provide an expression for the prefactor A and the exponents α and η . [Hint: convert the integral in r to spherical coordinates.]

Solution:

$$Z_1 = \int \exp[-E / kT] \text{ where } E = p^2 / 2m + V(r).$$

$$Z_1 = \frac{1}{h^3} \left(\int_{-\infty}^{\infty} \exp[-p_x^2 / 2mkT] dp_x \right) \left(\int_{-\infty}^{\infty} \exp[-p_y^2 / 2mkT] dp_y \right) \left(\int_{-\infty}^{\infty} \exp[-p_z^2 / 2mkT] dp_z \right) \\ \times \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^\infty dr \exp[-ar / kT] r^2 \sin \theta$$

Using equation sheet values for integrals leads to

$$Z_1 = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} (4\pi) 2 \left(\frac{kT}{a} \right)^3 = 8\pi k^3 \left(\frac{2\pi mk}{h^2} \right)^{3/2} T^{9/2} a^{-3} = AT^\alpha a^{-\eta}$$

- (b) Find an expression for the entropy S of this classical gas.

Solution:

$$\text{Use } F = -kT \ln Z \text{ with } Z = \frac{1}{N!} Z_1^N, \text{ then } S = - \left(\frac{\partial F}{\partial T} \right)_{N,V}$$

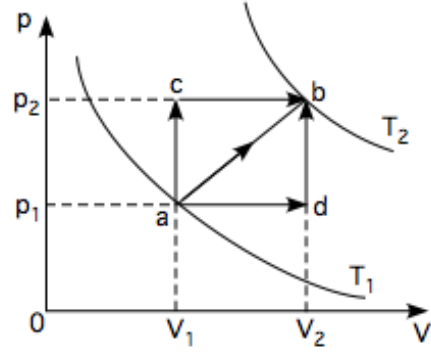
$$F = -kT [-\ln N! + N \ln Z_1] \approx -kT [-N \ln N + N + N \ln Z_1]$$

$$S = k [-N \ln N + N + N \ln Z_1] + kTN \left(\frac{\partial \ln Z_1}{\partial T} \right)_{N,V}, \text{ where } \left(\frac{\partial \ln Z_1}{\partial T} \right)_{N,V} = \frac{9}{2T}$$

$$S = kN \left[\frac{11}{2} + \ln \frac{Z_1}{N} \right]$$

Problem 2

A classical ideal gas is taken from state a to state b in the figure using three different paths: acb , adb , and ab . The pressure $p_2 = 2p_1$ and the volume $V_2 = 2V_1$.



- (a) The heat capacity $C_V = \frac{5}{2} Nk$. Starting from the First Law of Thermodynamics derive a value for C_p . No credit will be given for this part if you just state the answer.

Solution:

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p. \text{ From the first Law } dU = dQ - pdV, \text{ let } dQ = dU + pdV.$$

$$\text{Write } dU \text{ in terms of } V \text{ and } T \text{ as } dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV.$$

The internal energy of an ideal gas depends only on temperature, so $\left(\frac{\partial U}{\partial V} \right)_T = 0$.

$$\text{Combining these results leads to } dQ = \left(\frac{\partial U}{\partial T} \right)_V dT + pdV = C_V dT + pdV.$$

$$\text{Therefore, } C_p = \left(\frac{\partial Q}{\partial T} \right)_p = C_V + p \left(\frac{\partial V}{\partial T} \right)_p = C_V + Nk, \text{ the latter is obtained from } pV = NkT.$$

$$\text{So, } C_p = \frac{7}{2} Nk.$$

- (b) Compute the heat supplied to the gas along each of the three paths, acb , adb , and ab , in terms of N , k , and T_1 .

Solution:

Paths acb , and adb consist of constant pressure and constant volume processes.

$$\begin{aligned} Q(acb) &= \int_a^c C_V dT + \int_c^b C_p dT = \int_{p_1}^{p_2} \frac{5}{2} Nk \frac{V_1}{Nk} dp + \int_{V_1}^{V_2} \frac{7}{2} Nk \frac{p_2}{Nk} dV \\ &= \frac{5}{2} Nk \frac{V_1}{Nk} (p_2 - p_1) + \frac{7}{2} Nk \frac{p_2}{Nk} (V_2 - V_1) = \frac{5}{2} Nk \frac{V_1}{Nk} (p_1) + \frac{7}{2} Nk \frac{2p_1}{Nk} (V_1) = \frac{19}{2} NkT_1 \end{aligned}$$

$$\begin{aligned}
Q(adb) &= \int_a^d C_p dT + \int_d^b C_V dT + = \int_{V_1}^{V_2} \frac{7}{2} Nk \frac{p_1}{Nk} dV + \int_{p_1}^{p_2} \frac{5}{2} Nk \frac{V_2}{Nk} dp \\
&= \frac{7}{2} Nk \frac{p_1}{Nk} (V_2 - V_1) + \frac{5}{2} Nk \frac{V_2}{Nk} (p_2 - p_1) = \frac{7}{2} Nk \frac{p_1}{Nk} (V_1) + \frac{5}{2} Nk \frac{2V_1}{Nk} (p_1) = \frac{17}{2} NkT_1
\end{aligned}$$

The heat along path ab can be calculated by taking the difference between ΔU and W .

ΔU between states a and b can be calculated along any path because it is a state function.

W along path ab is also easy to calculate.

First, calculate $\Delta U = W + Q$ for any path. We already have $Q(adb)$, so

$$W(adb) = - \int_a^d p dV - \int_d^b p dV = - \int_{V_1}^{V_2} p_1 dV = -p_1 V_1 = -NkT_1$$

$$\Delta U = W(adb) + Q(adb) = \frac{17}{2} NkT_1 - NkT_1 = \frac{15}{2} NkT_1$$

$$\text{Now, for } W(ab) = - \int_a^b p dV = - \int_{V_1}^{V_2} p_1 \frac{V}{V_1} dV = - \frac{p_1}{2V_1} (V_2^2 - V_1^2) = - \frac{3p_1 V_1}{2} = - \frac{3}{2} NkT_1$$

$$Q(ab) = \Delta U - W(ab) = \frac{15}{2} NkT_1 - \left(- \frac{3}{2} NkT_1 \right) = 9NkT_1$$

(c) What is the heat capacity C_{ab} of the gas for the process ab ?

Solution:

$$C_{ab} = \left(\frac{dQ}{dT} \right)_{ab}, \text{ so consider } dQ = dU + p dV = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV + p dV = C_V dT + p dV$$

$$\therefore C_{ab} = C_V + p \left(\frac{dV}{dT} \right)_{ab}$$

$$\text{Derive an expression for } \left(\frac{dV}{dT} \right)_{ab} \text{ using } p = \frac{p_1}{V_1} V \text{ and } p = \frac{NkT}{V} \Rightarrow V^2 = \frac{NkTV_1}{p_1}$$

$$\text{differentiate: } 2VdV = \frac{NkV_1}{p_1} dT \text{ or } \left(\frac{dV}{dT} \right)_{ab} = \frac{NkV_1}{2Vp_1}$$

$$\therefore C_{ab} = C_V + p \frac{NkV_1}{2Vp_1} = C_V + \frac{Nk}{2} = 3Nk$$

Problem 3

Consider a one-dimensional stretched elastic string that is fixed at its two ends and vibrates only in a direction perpendicular to its length. The string consists of a very large number N of atoms arranged in a single row. Let the energies of vibration be quantized in units of hf , where f is the vibration frequency. This string is in thermal equilibrium with a heat bath at temperature T .

- (a) Determine an expression for the thermal energy of this string in terms of an integral over the variable $x = \varepsilon / kT$.

Solution:

The Planck distribution $\bar{n} = \frac{1}{e^{\varepsilon/kT} - 1}$

(note that equation sheet has general expression $\bar{n} = \frac{1}{e^{(\varepsilon-\mu)/kT} \pm 1}$).

$U = 2 \sum_n \frac{\varepsilon}{e^{\varepsilon/kT} - 1}$, where the 2 is from the two polarizations of vibrations and the energy levels

are given by $\varepsilon = hf = \frac{hc_s}{\lambda} = \frac{nhc_s}{2L}$, L is the length of the string and c_s is the speed of sound of the vibrations.

For N atoms in this string, we can write $U = 2 \int_0^N dn \frac{\varepsilon}{e^{\varepsilon/kT} - 1}$.

Let's rewrite this integral in terms of $x = \varepsilon / kT$ with the limit $x_{\max} = \frac{hc_s N}{2LkT}$.

$$U = 2 \left(\frac{2L}{hc_s} \right) (kT)^2 \int_0^{x_{\max}} dx \frac{x}{e^x - 1}$$

- (b) Identify a characteristic temperature that separates low T and high T behavior.

Determine an expression for the thermal energy of this string in the limit of low and high T . Comment on these results in the context of the equipartition theorem.

Solution:

Rewrite x_{\max} in terms of a characteristic temperature as $x_{\max} = \frac{hc_s N}{2LkT} = \frac{T_D}{T}$, where T_D is a characteristic (Debye) temperature for 1-d vibrations. Now, we can rewrite the energy integral

$$\text{as } U = \frac{2NkT^2}{T_D} \int_0^{T_D/T} dx \frac{x}{e^x - 1}.$$

At high T , we approximate $e^x \approx 1 + x$, so that

$$U \approx \frac{2NkT^2}{T_D} \int_0^{T_D/T} dx = \frac{2NkT^2}{T_D} \left(\frac{T_D}{T} \right) = 2NkT. \text{ This agrees with the equipartition result that}$$

assigns an average thermal energy of $\frac{1}{2}kT$ to each quadratic degree of freedom. The number of vibrational modes for each polarization of a 1-dimensional string of atoms approaches N for large N . Each mode has 2 degrees of freedom (one for the kinetic energy and one for the potential energy), plus there are two polarizations.

At low T , we let $T_D / T \rightarrow \infty$. The integral $\int_0^{\infty} dx \frac{x}{e^x - 1} = \frac{\pi^2}{6}$ (from equation sheet), so that

$$U \approx \frac{\pi^2 NkT^2}{3T_D}. \text{ Equipartition theorem does not say anything about this low } T \text{ result.}$$

Problem 4

Consider a spherical drop of liquid water containing N_l molecules surrounded by $N - N_l$ molecules of water vapor. The drop and its vapor may be out of equilibrium.

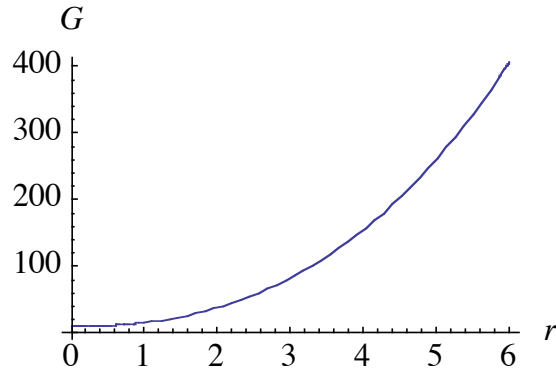
- (a) Neglecting surface effects write an expression for the Gibbs free energy of this system if the chemical potential of liquid water in the drop is μ_l and the chemical potential of water in the vapor is μ_v . Rewrite N_l in terms of the (constant) volume per molecule in the liquid, v_l , and the radius r of the drop.

Solution: $G = \mu_l N_l + \mu_v (N - N_l) = N\mu_v + N_l(\mu_l - \mu_v) = N\mu_v + \frac{4\pi r^3}{3v_l}(\mu_l - \mu_v)$

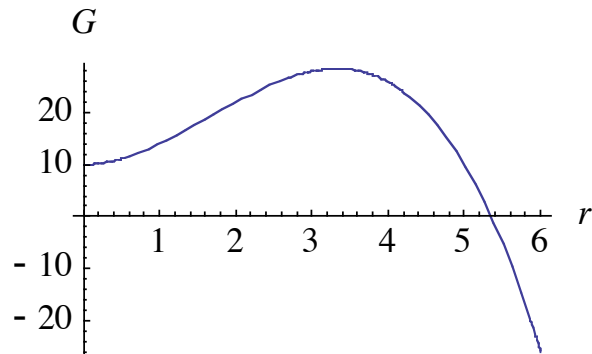
- (b) The effect of the surface of the drop can be included by adding a piece $G_{\text{surface}} = \sigma A$ to the free energy, where σ is the surface tension ($\sigma > 0$) and A is the surface area of the drop. Write G_{total} with the surface piece expressed in terms of r . Make two qualitative hand-sketches of G_{total} : one sketch with $(\mu_l - \mu_v) > 0$ and one sketch with $(\mu_l - \mu_v) < 0$. Describe the behavior of the drop in these two cases.

Solution: $G_{\text{total}} = N\mu_v + \frac{4\pi r^3}{3v_l}(\mu_l - \mu_v) + 4\pi\sigma r^2$

For $(\mu_l - \mu_v) > 0$, the drop radius is always zero, so the drop just evaporates.



For $(\mu_l - \mu_v) < 0$, the drop radius is either zero or the drop increases in size depending upon whether or not the radius is larger than a critical radius.



- (c) Under appropriate conditions, there is a critical radius, r_c , that separates drops which grow in size from those that shrink. Determine this critical radius.

Solution:

We saw in part (b) that for $(\mu_l - \mu_v) < 0$ the drop either evaporates completely or grows. The critical radius separates these two types of behaviors and can be determined from the maximum in G .

$$\left. \frac{dG}{dr} \right|_{r_c} = -\frac{4\pi r_c^2}{v_l}(\mu_v - \mu_l) + 8\pi\sigma r_c = 0$$

$$r_c = \frac{2\sigma v_l}{\mu_v - \mu_l}$$

- (d) Assume that the vapor behaves as an ideal gas and recall that the chemical potential of an ideal gas is given by $\mu_v = \mu_v^o + kT \ln(p / p^o)$. Write the chemical potential difference $(\mu_v - \mu_l)$ in terms of the vapor pressure and a reference pressure p^o , where p^o is taken to be the pressure of a vapor in equilibrium with a large flat surface of water. Then, derive and comment on the dependence of the relative humidity p / p^o on r_c .

Solution:

If p_o is the pressure of a vapor in equilibrium with a large flat surface of water, then the reference chemical potential is just the chemical potential of the bulk liquid, $\mu_v^o = \mu_l$.

Therefore, $\mu_v - \mu_l = kT \ln(p / p^o)$ and $r_c = \frac{2\sigma v_l}{kT \ln(p / p^o)}$.

So, $p / p^o = \exp(2\sigma v_l / kTr_c)$. Smaller critical radii require higher relative humidity, so drops grow more easily in a more humid environment.

Problem 5

Consider a paramagnetic material whose magnetic particles have angular momentum J , which is a multiple of $\frac{1}{2}$. The projections of the angular momentum along the z -axis can take $2J + 1$ values ($J_z = -J, -J + 1, -J + 2, \dots, J$), which leads to $2J + 1$ allowed values of the z -component of a particle's magnetic moment ($\mu_z = -J\delta_\mu, -(J+1)\delta_\mu, \dots, J\delta_\mu$). The energy of the magnetic moment in a magnetic field pointing in the $+z$ direction is $-\mu_z B$.

- (a) Derive an expression for the partition function Z_1 of a single magnetic particle in a magnetic field B pointing in the $+z$ direction. Write your answer in terms of hyperbolic sin functions, where $\sinh(x) = \frac{1}{2}(e^x - e^{-x})$. You may find it convenient to use the variable $b = \delta_\mu B\beta$, where $\beta = 1/kT$.

Solution:

The allowed energies are $E = J\delta_\mu B, (J+1)\delta_\mu B, \dots, -J\delta_\mu B$.

The partition function is

$$Z_1 = e^{-J\delta_\mu B\beta} + e^{-(J+1)\delta_\mu B\beta} + e^{-(J+2)\delta_\mu B\beta} + \dots + e^{J\delta_\mu B\beta}, \text{ where } \beta = 1/kT$$

Let $b = \delta_\mu B\beta$,

$$\begin{aligned} Z_1 &= e^{-Jb} + e^{-(J+1)b} + e^{-(J+2)b} + \dots + e^{Jb} \\ &= e^{-Jb} \left[1 + e^b + e^{2b} + \dots + e^{2Jb} \right] \\ &= e^{-Jb} \left[1 + e^b + (e^b)^2 + \dots + (e^b)^{2J} \right] \\ &= e^{-Jb} \left[\frac{1 - (e^b)^{2J+1}}{1 - e^b} \right] = \frac{e^{-Jb} - e^{(J+1)b}}{1 - e^b} \end{aligned}$$

To write this in terms of sinh functions,

$$Z_1 = \frac{e^{-Jb} - e^{(J+1)b}}{1 - e^b} \left(\frac{e^{-b/2}}{e^{-b/2}} \right) = \frac{e^{-(J+1/2)b} - e^{(J+1/2)b}}{e^{-b/2} - e^{b/2}} = \frac{\sinh[(J+1/2)b]}{\sinh(b/2)}$$

- (b) Derive an expression for the average energy of the particle in part (a). Write your answer in terms of the hyperbolic cotangent function $\coth(x) = \frac{\cosh(x)}{\sinh(x)}$.

Solution:

$$\begin{aligned}\bar{E} &= -\frac{1}{Z} \frac{dZ}{d\beta} = -\frac{1}{Z} \frac{db}{d\beta} \frac{dZ}{db} \\ &= -\frac{\sinh(b/2)}{\sinh[(J+1/2)b]} (\delta_\mu B) \frac{\left(J + \frac{1}{2}\right) \sinh \frac{b}{2} \cosh \left[b \left(J + \frac{1}{2}\right)\right] - \frac{1}{2} \sinh \left[b \left(J + \frac{1}{2}\right)\right] \cosh \frac{b}{2}}{\left(\sinh \frac{b}{2}\right)^2} \\ &= -\delta_\mu B \left[\left(J + \frac{1}{2}\right) \coth \left[b \left(J + \frac{1}{2}\right)\right] - \frac{1}{2} \coth \frac{b}{2} \right]\end{aligned}$$

- (c) Use the expression for the average energy in part (b) to determine the magnetization M (the average z -component of the total magnetic moment) of a system of N identical, independent magnetic particles. Comment on its behavior as $T \rightarrow 0$.

Solution:

The average z -component of the magnetic moment of a single particle is just the average energy times $-1/B$. The total M will be the average energy times $-N/B$.

$$M = N\delta_\mu \left[\left(J + \frac{1}{2}\right) \coth \left[b \left(J + \frac{1}{2}\right)\right] - \frac{1}{2} \coth \frac{b}{2} \right]$$

As $T \rightarrow 0$, $b \rightarrow \infty$, and the coth functions go to 1, so $M = NJ\delta_\mu$. This is equivalent to having all N particles in their lowest energy magnetic state with $\mu_z = J\delta_\mu$.