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

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

\[\int_{0}^{\infty} x^2 \exp[-bx^2] \, dx = \frac{1}{4} \sqrt{\frac{\pi}{b^3}}\]

\[\int_{0}^{\infty} x \, dx = 2\]

\[\int_{0}^{\infty} x \, \frac{x}{e^x - 1} \, dx = \frac{\pi^2}{6}\]

\[\int_{0}^{\infty} x \, \frac{x}{e^x + 1} \, dx = \frac{\pi^2}{12}\]

\[\int_{0}^{\infty} \frac{x^2}{e^x - 1} \, dx = 2 \zeta(3), \text{ where } \zeta(3) \text{ can be considered to be just a number.}\]

\[\int_{0}^{\infty} \frac{x^2}{e^x + 1} \, dx = \frac{3}{2} \zeta(3)\]

\[\bar{n} = \frac{1}{e^{(e-\mu)/kt} \pm 1}\]

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

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

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

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

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

\[\sum_{m=0}^{n} x^m = \frac{1 - x^{n+1}}{1-x}\]
Problem 1

A gas of \( N \) identical classical non-interacting atoms is held in a potential \( V(r) = ar \), where \( r = \left( x^2 + y^2 + z^2 \right)^{1/2} \). 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 \( \alpha \) and \( \eta \). [Hint: convert the integral in \( r \) to spherical coordinates.]

Solution:

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

\[
Z_1 = \frac{1}{\hbar^3} \left( \int_{-\infty}^{\infty} \exp[-p_x^2 / 2mkT] \, dp_x \right) \left( \int_{-\infty}^{\infty} \exp[-p_y^2 / 2mkT] \, dp_y \right) \left( \int_{-\infty}^{\infty} \exp[-p_z^2 / 2mkT] \, dp_z \right) \\
\times \pi \frac{2\pi}{0} \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} d\theta \, d\phi \, dr \exp[-ar / kT] r^2 \sin \theta
\]

Using equation sheet values for integrals leads to

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

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

Solution:

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

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

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

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

A classical ideal gas is taken from state \( a \) to state \( b \) in the figure using three different paths: \( abc \), \( adb \), 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:

\[
C_p = \left( \frac{\partial Q}{\partial T} \right)_p .
\]

From the first Law \( dU = dQ - pdV \), let \( dQ = dU + pdV \).

Write \( dU \) in terms of \( V \) and \( T \) 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 \( \left( \frac{\partial U}{\partial V} \right)_T = 0 \).

Combining these results leads to

\[
dQ = \left( \frac{\partial U}{\partial T} \right)_V \, dT + pdV = C_v dT + pdV.
\]

Therefore,

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

So,

\[
C_p = \frac{7}{2}Nk.
\]

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

Solution:

Paths \( abc \), and \( adb \) consist of constant pressure and constant volume processes.

\[
Q(abc) = \int_a^c C_v \, dT + \int_c^b C_p \, dT = \int_{p_1}^{p_2} \frac{5}{2}Nk \frac{V_1}{Nk} \, dp + \int_{V_1}^{V_2} \frac{7}{2}Nk \frac{p_2}{Nk} \, dV
\]

\[
= \frac{5}{2}Nk \frac{V_1}{Nk} (p_2 - p_1) + \frac{7}{2}Nk \frac{p_2}{Nk} (V_2 - V_1) = \frac{5}{2}Nk \frac{V_1}{Nk} (p_1) + \frac{7}{2}Nk \frac{p_1}{Nk} (V_1) = \frac{19}{2}Nk T_1
\]
$$Q(ab) = \int_{a}^{b} C_p \, dT + \int_{a}^{b} C_V \, dV = \int_{V_1}^{V_2} \frac{7}{2} Nk \frac{p_1}{Nk} \, dV + \int_{p_1}^{p_2} \frac{5}{2} Nk \frac{V_2}{Nk} \, dp$$

$$= \frac{7}{2} Nk \frac{p_1}{Nk} (V_2 - V_1) + \frac{5}{2} Nk \frac{V_2}{Nk} (p_2 - p_1) = \frac{7}{2} Nk \frac{p_1}{Nk} (V_1) + \frac{5}{2} Nk \frac{2V_1}{Nk} (p_1) = \frac{17}{2} Nk T_1$$

The heat along path \(ab\) can be calculated by taking the difference between \(\Delta U\) and \(W\).

\(\Delta U\) 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 \(Q(ab)\), so

\[ W(ab) = -\int_{a}^{b} p \, dV - \int_{a}^{b} dV = -\int_{V_1}^{V_2} p_1 \, dV = -p_1 V_1 = -Nk T_1 \]

\[ \Delta U = W(ab) + Q(ab) = \frac{17}{2} Nk T_1 - Nk T_1 = \frac{15}{2} Nk T_1 \]

Now, for \(W(ab) = -\int_{a}^{b} p \, dV = -\int_{V_1}^{V_2} p_1 \, dV = \frac{V_2}{V_1} p_1 (V_2 - V_1) = -\frac{3}{2} Nk T_1 \]

\[ Q(ab) = \Delta U - W(ab) = \frac{15}{2} Nk T_1 - \left(-\frac{3}{2} Nk T_1\right) = 9 Nk T_1 \]

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

Solution:

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

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

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

differentiate: \(2V dV = \frac{Nk V_1}{p_1} dT \) or \( \left(\frac{dV}{dT}\right)_{ab} = \frac{Nk V_1}{2 V p_1} \)

\[ \therefore C_{ab} = C_V + p \frac{Nk V_1}{2 V p_1} = C_V + \frac{Nk}{2} = 3 Nk \]
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 \( x = \frac{\varepsilon}{kT} \).

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 \( \varepsilon = hf = \frac{h c_s}{\lambda} = \frac{nh c_s}{2L} \), \( L \) 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 

\[
U = 2 \int_{0}^{N} d\bar{n} \frac{\varepsilon}{e^{\varepsilon/kT} - 1}.
\]

Let’s rewrite this integral in terms of \( x = \frac{\varepsilon}{kT} \) with the limit \( x_{\text{max}} = \frac{hc_s N}{2LkT} \).

\[
U = 2 \left( \frac{2L}{hc_s} \right)^2 (kT)^2 \int_{0}^{x_{\text{max}}} dx \frac{x}{e^x - 1}
\]

(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 \( x_{\text{max}} \) in terms of a characteristic temperature as \( x_{\text{max}} = \frac{hc_s N}{2LkT} = \frac{T_D}{T} \), where \( T_D \) is a characteristic (Debye) temperature for 1-d vibrations. Now, we can rewrite the energy integral
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
\[
U \approx \frac{2NkT^2}{T_D} \int_0^{T_D/T} dx = \frac{2NkT^2}{T_D} \left( \frac{T_D}{T} \right) = 2NkT.
\]
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 \( T_D / T \to \infty \). The integral
\[
\int_0^{\infty} dx \frac{x}{e^x - 1} = \frac{\pi^2}{6}
\]
(from equation sheet), so that
\[
U = \frac{\pi^2 NkT^2}{3T_D}.
\]
Equipartition theorem does not say anything about this low \( T \) 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 $\mu_l$ and the chemical potential of water in the vapor is $\mu_v$. 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 $\sigma$ is the surface tension ($\sigma > 0$) and $A$ is the surface area of the drop. Write $G_{\text{total}}$ with the surface piece expressed in terms of $r$. Make two qualitative hand-sketches of $G_{\text{total}}$: 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 $G$.

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

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

(d) Assume that the vapor behaves as an ideal gas and recall that the chemical potential of an
ideal gas is given by $\mu_v = \mu_v^0 + kT \ln(p / p^o)$. 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, $\mu_v^0 = \mu_l$.

Therefore, $\mu_v - \mu_l = kT \ln(p / p^o)$ and

$$r_c = \frac{2\sigma \nu_l}{kT \ln(p / p^o)}.$$  

So, $p / p^o = \exp(2\sigma \nu_l / kTr_c)$. Smaller critical radii require higher relative humidity, so
drops grow more easily in a more humid environment.
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 ($J_z = -J, -J + 1, -J + 2, \ldots, J$), which leads to $2J - 1$ allowed values of the $z$-component of a particle’s magnetic moment ($\mu_z = -J\delta_{\mu}, -(J+1)\delta_{\mu}, \ldots, J\delta_{\mu}$). 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 $\beta = 1/\kappa T$.

Solution:

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

The partition function is

$$Z_1 = e^{-J\delta_{\mu} B\beta} + e^{-(J+1)\delta_{\mu} B\beta} + e^{-(J+2)\delta_{\mu} B\beta} + \ldots + e^{J\delta_{\mu} B\beta},$$

where $b = \delta_{\mu} B\beta$.

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

$$Z_1 = e^{-Jb} + e^{-(J+1)b} + e^{-(J+2)b} + \ldots + e^{Jb}$$

$$= e^{-Jb} \left[ 1 + e^b + e^{2b} + \ldots + e^{2Jb} \right]$$

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

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

To write this in terms of sinh functions,

$$Z_1 = \frac{e^{-Jb} - e^{(J+1)b}}{1 - e^b} \left( \frac{e^{b/2}}{e^{b/2}} \right) = \frac{e^{-(J+1/2)b} - e^{(J+1/2)b}}{e^{-b/2} - e^{b/2}} = \frac{\sinh \left( (J + 1/2)b \right)}{\sinh (b/2)}$$
(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:
\[
\bar{E} = -\frac{1}{Z} \frac{dZ}{d\beta} = -\frac{1}{Z} \frac{db}{d\beta} \frac{dZ}{db} = -\frac{\sinh(b/2)}{\sinh[(J+1/2)b]} \left( \delta \mu B \right) \left( J + \frac{1}{2} \right) \cosh \left( \frac{b}{2} \left( J + \frac{1}{2} \right) \right) - \frac{1}{2} \sinh \left( \frac{b}{2} \left( J + \frac{1}{2} \right) \right) \cosh \left( \frac{b}{2} \right) \frac{1}{\left( \sinh \left( \frac{b}{2} \right) \right)^2} \\
= -\delta \mu B \left[ \left( J + \frac{1}{2} \right) \coth \left( \frac{b}{2} \right) \left( J + \frac{1}{2} \right) - \frac{1}{2} \coth \left( \frac{b}{2} \right) \right]
\]

(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 \( T \to 0 \).

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 \(-N/B\).

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

As \( T \to 0 \), \( b \to \infty \), 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 \( \mu_z = J\delta \mu \).