University of Illinois at Chicago
Department of Physics

Thermodynamics and Statistical Physics
Qualifying Exam

January ?, 2012
9:00am-12:00pm

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

Mathematical Formulae

Notation:

$$\beta = \frac{1}{k_B T}$$

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z dx \exp(-x^2) \qquad \text{erf is known as the error function}$$

$$\text{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty dx \exp(-x^2) \qquad \text{erfc is known as the complimentary error function}$$

Integrals:

$$\int dx \ln x = x \ln x - x$$

$$\int \frac{dx}{x} = \ln x$$

$$\int_b^\infty dx \exp(-ax^2) = \frac{1}{2} \sqrt{\frac{\pi}{a}} \, \text{erfc}\left(\sqrt{a}\, b\right)$$

$$\int_0^a dx \, \text{erfc}(x) = \frac{1 - \exp(-a^2)}{\sqrt{\pi}} + a \, \text{erfc}(a)$$

$$\int_0^n dx \, x^{1/2} \exp(-x) = \frac{\sqrt{\pi}}{2} \text{erf}\left(\sqrt{n}\right) - \sqrt{n} \exp(-n)$$

$$\int_0^n x^{3/2} \exp(-x) = \frac{3}{4} \text{erf}(\sqrt{n}) - \frac{1}{2} \sqrt{n} \exp(-n)(3 + 2n)$$

Expansions:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots \qquad \text{for } x < 1$$

$$\exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

$$\text{erfc}(x) = \exp(-x^2)\left[\frac{1}{\sqrt{\pi}\, x} + \dots\right] \qquad \text{for } x \to \infty$$

$$\sinh(x) = x + \dots \qquad \text{for } x \to 0$$

$$\cosh(x) = 1 + \dots \qquad \text{for } x \to 0$$

Problem 1

Consider a system consisting of N non-interacting particles each with isospin $I = 3/2$. The energies of the states with different I_z are given by

$$E(I_z = -3/2) = E_1; \qquad E(I_z = -1/2) = E_2$$
$$E(I_z = 1/2) = E_3; \qquad E(I_z = 3/2) = E_3$$

with $E_1 < E_2 < E_3$ and $\Delta_{12} = E_2 - E_1 \ll \Delta_{23} = E_3 - E_2$.

a) Without using the partition function, give the value of the total energy, $\langle E \rangle$, at temperatures $T = 0$, $\Delta_{12} \ll T \ll \Delta_{23}$, and $\Delta_{23} \ll T$. Provide a justification for your results. Sketch $\langle E \rangle$ as a function of temperature.

b) What is the occupation of the I_z-states for temperature $T \to \infty$ Without using the partition function, give a value of the specific heat for temperature $T \to \infty$? Provide a justification for your results.

c) Without using the partition function, give the value of the average isospin per particle, $\langle I_z \rangle$, at temperatures $T = 0$, $\Delta_{12} \ll T \ll \Delta_{23}$, and $\Delta_{23} \ll T$. Provide a justification for your results. Sketch $\langle I_z \rangle$ as a function of temperature.

d) Using the partition function, compute the average isospin per particle, $\langle I_z \rangle$, in the limit $T \to \infty$. How does you result relate to those in part c)?

Solutions:

a) At $T = 0$, all particles are in the ground state, and hence $\langle E \rangle = NE_1$. For $\Delta_{12} \ll T \ll \Delta_{23}$, the two lowest states are equally populated, while the two higher energy states are empty, and thus $\langle E \rangle = N(E_1 + E_2)/2$. For $\Delta_{23} \ll T$, all states are equally populated, and hence $\langle E \rangle = N(E_1 + E_2 + 2E_3)/4$.

b) For $T \to \infty$, all I_z-states are equally populated with $N/4$ particles being in each of these four states. Hence, by increasing temperature, no more energy can be stored in the system, and hence $C \to 0$ as $T \to \infty$.

c) At $T = 0$, all particles are in the ground state, and hence $\langle I_z \rangle = -3N/2$. For $\Delta_{12} \ll T \ll \Delta_{23}$, the two lowest states are equally populated, while the two higher energy states are empty, and thus $\langle I_z \rangle = N/2(-3/2 - 1/2) = -N$. For $\Delta_{23} \ll T$, all states are equally populated, and hence $\langle I_z \rangle = 0$.

d) The partition function is given by

$$Z = e^{-\beta E_1} + e^{-\beta E_2} + 2e^{-\beta E_3}$$

and hence

$$
\begin{aligned}
\langle I_z \rangle &= \frac{N}{Z}\left[\left(-\frac{3}{2}\right)e^{-\beta E_1} + \left(-\frac{1}{2}\right)e^{-\beta E_2} + \left(\frac{1}{2}\right)e^{-\beta E_3} + \left(\frac{3}{2}\right)e^{-\beta E_3}\right] \\
&= N\frac{\left(-\frac{3}{2}\right) + \left(-\frac{1}{2}\right)e^{-\beta(E_2 - E_1)} + \left(\frac{1}{2}\right)e^{-\beta(E_3 - E_1)} + \left(\frac{3}{2}\right)e^{-\beta(E_3 - E_1)}}{1 + e^{-\beta(E_2 - E_1)} + 2e^{-\beta(E_3 - E_1)}} \\
&= 0
\end{aligned}
$$

since $\beta \to 0$. This agrees with the result in c).

Problem 2

Consider an ideal gas of N_0 non-interacting spin-less particles each with kinetic energy

$$\varepsilon = \frac{m}{2}\vec{v}^2$$

that is contained in a box. The temperature of the gas is T, and the particles are uniformly distributed throughout the box.

a) What is the normalized velocity distribution of the gas?

b) What is the total energy, $E_0 = \langle E \rangle$ of all particles in the box?

c) Instantaneously remove all particles from the gas that possess a kinetic energy larger than nk_BT (n is an arbitrary real, positive number). How many particles remain in terms of N_0? What is the new total energy, E_{new} in terms of E_0? After the remaining particles have returned to equilibrium, what is the new temperature, T_{new} of the gas in terms of T? For which n does one obtain $T_{new} = T/2$?

Solutions:

a)

$$P(\vec{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{m\vec{v}^2}{2k_B T} \right)$$

b) Due to the equipartition theorem

$$\langle \varepsilon \rangle = \frac{m}{2}\langle \vec{v}^2 \rangle = \frac{3}{2}k_B T$$

and hence

$$E_0 = \langle E \rangle = \frac{3}{2}Nk_B T$$

c) We instantaneously removed all particles with a kinetic energy

$$\varepsilon_{kin} = \frac{1}{2}mv^2 \geq nk_B T$$

The number of remaining particle, N_{new}, is given by

$$N_{new} = N_0 \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int' d^3v \exp\left[-\frac{mv^2}{2k_B T} \right]$$

$$= N_0 \left(\frac{m}{2\pi k_B T} \right)^{3/2} 4\pi \int_0^{v_c} dv\, v^2 \exp\left[-\frac{mv^2}{2k_B T} \right]$$

where

$$v_c = \sqrt{\frac{2nk_B T}{m}}$$

I next perform the variable transformation

$$x = \frac{mv^2}{2k_BT} \Rightarrow dx = \frac{mv}{k_BT}dv = \frac{m}{k_BT}\sqrt{\frac{2k_BTx}{m}}\,dv = \sqrt{\frac{2mx}{k_BT}}\,dv$$

and thus

$$N_{new} = N_0\left(\frac{m}{2\pi k_BT}\right)^{3/2} 4\pi\sqrt{\frac{k_BT}{2m}} \int_0^n dx\, \frac{2k_BT}{m}x^{1/2}\exp[-x]$$

$$= N_0\frac{2}{\sqrt{\pi}} \int_0^n dx\, x^{1/2}\exp[-x]$$

$$= N_0\frac{2}{\sqrt{\pi}}\left[\frac{\sqrt{\pi}}{2}\,\mathrm{erf}(\sqrt{n}) - \sqrt{n}\,\exp(-n)\right]$$

Next, we compute the remaining energy that is contained in the system after the particles are removed.

$$E_{new} = N_0\left(\frac{m}{2\pi k_BT}\right)^{3/2} \int' d^3v\left(\frac{1}{2}mv^2\right)\exp\left[-\frac{mv^2}{2k_BT}\right]$$

$$= N_0\left(\frac{m}{2\pi k_BT}\right)^{3/2}\frac{m}{2}4\pi \int_0^{v_c} dv\, v^4\exp\left[-\frac{mv^2}{2k_BT}\right]$$

I next perform the variable transformation

$$x = \frac{mv^2}{2k_BT} \Rightarrow dx = \frac{mv}{k_BT}dv = \frac{m}{k_BT}\sqrt{\frac{2k_BTx}{m}}\,dv = \sqrt{\frac{2mx}{k_BT}}\,dv$$

and thus

$$E_{new} = N_0\left(\frac{m}{2\pi k_BT}\right)^{3/2}\frac{m}{2}4\pi\sqrt{\frac{k_BT}{2m}} \int_0^n dx\left(\frac{2k_BT}{m}\right)^2 x^{3/2}\exp[-x]$$

$$= N_0\frac{2k_BT}{\sqrt{\pi}} \int_0^n dx\, x^{3/2}\exp[-x]$$

$$= N_0\frac{k_BT}{2\sqrt{\pi}}\left[3\sqrt{\pi}\,\mathrm{erf}(\sqrt{n}) - 6\sqrt{n}\,\exp(-n) - 4n^{3/2}\exp(-n)\right]$$

After equilibration, the new temperature is given by

$$E_{new} = \frac{3}{2}N_{new}k_BT_{new}$$

or

$$T_{new}(n) = \frac{2}{3}\frac{E_{new}}{k_BN_{new}} = \frac{2}{3}\frac{N_0\frac{k_BT}{2\sqrt{\pi}}\left[3\sqrt{\pi}\,\mathrm{erf}(\sqrt{n}) - 6\sqrt{n}\,\exp(-n) - 4n^{3/2}\exp(-n)\right]}{k_BN_0\frac{2}{\sqrt{\pi}}\left[\frac{\sqrt{\pi}}{2}\,\mathrm{erf}(\sqrt{n}) - \sqrt{n}\,\exp(-n)\right]}$$

$$= \frac{1}{6}\frac{3\sqrt{\pi}\,\mathrm{erf}(\sqrt{n}) - 6\sqrt{n}\,\exp(-n) - 4n^{3/2}\exp(-n)}{\frac{\sqrt{\pi}}{2}\,\mathrm{erf}(\sqrt{n}) - \sqrt{n}\,\exp(-n)}T$$
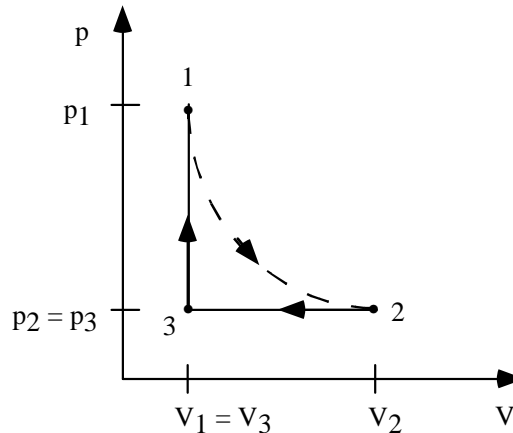
and thus

$$T_{new} = T/2$$

requires

$$\frac{1}{6} \frac{3\sqrt{\pi}\ \mathrm{erf}(\sqrt{n}\ ) - 6\sqrt{n}\ \exp(-n) - 4n^{3/2}\exp(-n)}{\frac{\sqrt{\pi}}{2}\ \mathrm{erf}(\sqrt{n}\ ) - \sqrt{n}\ \exp(-n)} = \frac{1}{2}$$

and thus

$$n = 1.527$$

Problem 3

Suppose one mole of an ideal gas is subjected to the cyclic process shown below (with temperature V_1, V_2 and V_3 in states $1, 2$ and 3, respectively)

$1 \Rightarrow 2$ is an isothermal expansion.
$2 \Rightarrow 3$ is an isobaric expansion.
$3 \Rightarrow 1$ is an isochoric heating step.
All steps are reversible

a) What is the change in internal energy, ΔU, for the entire cyclic process $1 \Rightarrow 2 \Rightarrow 3 \Rightarrow 1$.

b) Use the First Law of Thermodynamics to calculate ΔU, δQ, and δW for the process $1 \Rightarrow 2$.

c) Use the First Law of Thermodynamics to calculate ΔU, δQ, and δW for the process $2 \Rightarrow 3$.

d) Use the First Law of Thermodynamics to calculate ΔU, δQ, and δW for the process $3 \Rightarrow 1$.

e) Is the total work done in a cycle positive or negative? What is the efficiency, η, of this cycle? In which limit does one obtain $\eta = 1$.

Solutions:

a) Since we have carried out a cyclic process, namely $1 \Rightarrow 2 \Rightarrow 3 \Rightarrow 1$ we must have $\Delta U = 0$, or

$$Q_{1\Rightarrow 2} + W_{1\Rightarrow 2} + Q_{2\Rightarrow 3} + W_{2\Rightarrow 3} + Q_{3\Rightarrow 1} + W_{3\Rightarrow 1} = 0$$

b) Since this is an isothermal expansion, we have

$$\Delta U_{1\Rightarrow 2} = Q_{1\Rightarrow 2} + W_{1\Rightarrow 2} = 0$$

and thus

$$Q_{1\Rightarrow2} = -W_{1\Rightarrow2} = Nk_BT_1 \ln\left(\frac{V_2}{V_1}\right)$$

c)

$$Q_{2\Rightarrow3} = \int_{T_2}^{T_3} C_p \, dT = C_p(T_3 - T_2) < 0$$

$$W_{2\Rightarrow3} = -\int_{V_2}^{V_3} p_2 \, dV = p_2(V_2 - V_3) = \frac{Nk_BT_2}{V_2}(V_2 - V_1) = Nk_BT_1\left(1 - \frac{V_1}{V_2}\right)$$

$$\Delta U_{2\Rightarrow3} = Q_{2\Rightarrow3} + W_{2\Rightarrow3}$$

d) We have $W_{3\Rightarrow1} = 0$ since there is no change in volume, but

$$Q_{3\Rightarrow1} = \int_{T_3}^{T_1} C_V \, dT = C_V(T_1 - T_3)$$

$$\Delta U_{3\Rightarrow1} = Q_{3\Rightarrow1}$$

Let us check that

$$\Delta U_{tot} = 0$$

I have

$$\Delta U_{1\Rightarrow2} = 0$$

$$\Delta U_{2\Rightarrow3} = C_p(T_3 - T_2) + Nk_BT_1\left(1 - \frac{V_1}{V_2}\right)$$

$$\Delta U_{3\Rightarrow1} = C_V(T_1 - T_3)$$

and thus

$$\Delta U_{tot} = C_p(T_3 - T_2) + Nk_BT_1\left(1 - \frac{V_1}{V_2}\right) + C_V(T_1 - T_3)$$

$$= \frac{5}{2}Nk_B(T_3 - T_1) + Nk_BT_1\left(1 - \frac{V_1}{V_2}\right) + \frac{3}{2}Nk_B(T_1 - T_3)$$

$$= Nk_BT_3 - Nk_BT_1\frac{V_1}{V_2} = Nk_BT_3 - Nk_BT_2\frac{V_3}{V_2}$$

$$= Nk_B\left(\frac{T_3}{V_3} - \frac{T_2}{V_2}\right)V_3 = (p_3 - p_2)V_3 = 0$$

e) The total work done is

$$W_{tot} = W_{1\Rightarrow2} + W_{2\Rightarrow3} + W_{3\Rightarrow1} = -Nk_BT_1 \ln\left(\frac{V_2}{V_1}\right) + Nk_BT_1\left(1 - \frac{V_1}{V_2}\right)$$

$$= Nk_BT_1\left[1 - \frac{V_1}{V_2} - \ln\left(\frac{V_2}{V_1}\right)\right] < 0$$

Thus the system is performing work.

The efficiency is defined via

$$\eta = \frac{|W_{tot}|}{Q_{in}} = \frac{Nk_BT_1\left[\ln\left(\frac{V_2}{V_1}\right) - \left(1 - \frac{V_1}{V_2}\right)\right]}{Nk_BT_1\ln\left(\frac{V_2}{V_1}\right)} = 1 - \frac{1 - \frac{V_1}{V_2}}{\ln\left(\frac{V_2}{V_1}\right)}$$

One obtains $\eta = 1$ for $\frac{V_1}{V_2} \to 0$.

Problem 4

Consider a system consisting of M non-interacting molecules at temperature T. Each of these molecules possesses vibrations with energies

$$E_n = \hbar\omega_0\left(n + \frac{1}{2}\right) \quad \text{where} \quad n = 0, 1, 2, 3, \ldots, N_0$$

Let us first consider the case $N_0 = \infty$

a) Using the partition function, compute the total energy, $\langle E \rangle$, of the system for temperature $T \to 0$ and $T \to \infty$. Explain your results. At what temperature occurs the crossover from the $T \to 0$ to the $T \to \infty$ behavior of $\langle E \rangle$?

b) Compute $\langle n \rangle$ for $T \to \infty$. What is the physical interpretation of $\langle n \rangle$? What is the relation of $\langle n \rangle$ to the partition function and to $\langle E \rangle$?

c) Consider next the case where N_0 is a finite, integer number (i.e., $N_0 < \infty$). What is now the form of $\langle E \rangle$ for temperature $T \to \infty$?

d) Compute the specific heat, C_V, of the system in the limit $T \to \infty$ for the two cases $N_0 = \infty$ and $N_0 < \infty$. Explain the difference in C_V between these two cases.

Solutions:

a) Since the molecules do not interact with each other, the partition function of a single molecule is

$$Z_1 = \sum_{n=0}^{\infty} \exp\left[-\beta\hbar\omega_0\left(n + \frac{1}{2}\right)\right] = \exp\left[-\frac{\beta\hbar\omega_0}{2}\right]\sum_{n=0}^{\infty}(\exp[-\beta\hbar\omega_0])^n$$

$$= \exp\left[-\frac{\beta\hbar\omega_0}{2}\right]\frac{1}{1 - \exp[-\beta\hbar\omega_0]} = \frac{1}{\exp\left[\frac{\beta\hbar\omega_0}{2}\right] - \exp\left[-\frac{\beta\hbar\omega_0}{2}\right]}$$

$$= \frac{1}{2\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

The partition function of the entire system is then

$$Z_M = Z_1^M = 2^{-M}\frac{1}{\sinh^M\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

The average energy is given by

$$\langle E \rangle = -\frac{\partial}{\partial\beta}\ln Z_M = -\frac{M}{Z_1}\frac{\partial}{\partial\beta}\frac{1}{2\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]} = \frac{M}{2Z_1}\frac{\hbar\omega_0}{2}\frac{\cosh\left[\frac{\beta\hbar\omega_0}{2}\right]}{\sinh^2\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

$$= \frac{M}{2}2\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]\frac{\hbar\omega_0}{2}\frac{\cosh\left[\frac{\beta\hbar\omega_0}{2}\right]}{\sinh^2\left[\frac{\beta\hbar\omega_0}{2}\right]} = M\frac{\hbar\omega_0}{2}\frac{\cosh\left[\frac{\beta\hbar\omega_0}{2}\right]}{\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

$$= M\frac{\hbar\omega_0}{2}\frac{1}{\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

For $T \to 0$, we expand $\langle E \rangle$ in the limit $\beta \to \infty$ which yields

$$\langle E \rangle = M\frac{\hbar\omega_0}{2}\frac{1}{\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]} \approx M\frac{\hbar\omega_0}{2}$$

Hence each molecule has the energy $\frac{\hbar\omega_0}{2}$ associated with the zero-point fluctuations.

For $T \to \infty$, we expand $\langle E \rangle$ in the limit $\beta \to 0$ which yields

$$\langle E \rangle = M\frac{\hbar\omega_0}{2}\frac{1}{\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]} = M\frac{\hbar\omega_0}{2}\frac{\cosh\left[\frac{\beta\hbar\omega_0}{2}\right]}{\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]} = M\frac{\hbar\omega_0}{2}\frac{\exp\left[\frac{\beta\hbar\omega_0}{2}\right]+\exp\left[-\frac{\beta\hbar\omega_0}{2}\right]}{\exp\left[\frac{\beta\hbar\omega_0}{2}\right]-\exp\left[-\frac{\beta\hbar\omega_0}{2}\right]}$$

$$\approx M\frac{\hbar\omega_0}{2}\frac{2}{2\frac{\beta\hbar\omega_0}{2}} = \frac{M}{\beta} = Mk_BT$$

This is the classical result expected from the equipartition theorem. The crossover between these two limits occurs at $\frac{\beta\hbar\omega_0}{2} \approx 1$.

b) We have

$$\langle E \rangle = M\hbar\omega_0\left(\langle n \rangle + \frac{1}{2}\right) = M\,k_BT$$

and thus

$$\langle n \rangle + \frac{1}{2} = \frac{k_BT}{\hbar\omega_0}$$

and hence for $\frac{k_BT}{\hbar\omega_0} \gg 1$, I obtain

$$\langle n \rangle \approx \frac{k_BT}{\hbar\omega_0}$$

The excitation of each quantum n of oscillation requires the energy $\hbar\omega_0$.

c)

In this case, we have

$$\langle E \rangle = \frac{\sum_{n=0}^{N_0}\hbar\omega_0\left(n+\frac{1}{2}\right)\exp\left[-\beta\hbar\omega_0\left(n+\frac{1}{2}\right)\right]}{\sum_{n=0}^{N_0}\exp\left[-\beta\hbar\omega_0\left(n+\frac{1}{2}\right)\right]} = \frac{\sum_{n=0}^{N_0}\hbar\omega_0\left(n+\frac{1}{2}\right)\exp\left[-\beta\hbar\omega_0 n\right]}{\sum_{n=0}^{N_0}\exp\left[-\beta\hbar\omega_0 n\right]}$$

$$= \frac{\sum_{n=0}^{N_0}\hbar\omega_0\left(n+\frac{1}{2}\right)}{\sum_{n=0}^{N_0}1} = \frac{\hbar\omega_0}{N_0+1}\left[\frac{1}{2}(N_0+1)+N_0\frac{(N_0+1)}{2}\right]$$

$$= \frac{\hbar\omega_0}{2}[1+N_0]$$

Or Alternatively,

$$Z_1 = \sum_{n=0}^{N_0} \exp\left[-\beta\hbar\omega_0\left(n + \tfrac{1}{2}\right)\right] = \exp\left[-\frac{\beta\hbar\omega_0}{2}\right]\sum_{n=0}^{N_0}(\exp[-\beta\hbar\omega_0])^n$$

$$= \exp\left[-\frac{\beta\hbar\omega_0}{2}\right]\left[\sum_{n=0}^{\infty}(\exp[-\beta\hbar\omega_0])^n - \sum_{n=N_0+1}^{\infty}(\exp[-\beta\hbar\omega_0])^n\right]$$

$$= \exp\left[-\frac{\beta\hbar\omega_0}{2}\right]\left[\frac{1}{1-\exp[-\beta\hbar\omega_0]} - \sum_{n=0}^{\infty}(\exp[-\beta\hbar\omega_0])^{n+N_0+1}\right]$$

$$= \exp\left[-\frac{\beta\hbar\omega_0}{2}\right]\frac{1-(\exp[-\beta\hbar\omega_0])^{N_0+1}}{1-\exp[-\beta\hbar\omega_0]} = \frac{1-\exp[-(N_0+1)\beta\hbar\omega_0]}{2\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

The partition function of the entire system is then

$$Z_M = Z_1^M$$

The average energy is given by

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z_M = -\frac{M}{Z_1}\frac{\partial}{\partial\beta}\left\{\frac{1-\exp[-(N_0+1)\beta\hbar\omega_0]}{2\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]}\right\}$$

$$= -\frac{M}{2Z_1}\frac{(N_0+1)\hbar\omega_0\exp[-(N_0+1)\beta\hbar\omega_0]\sinh\left[\frac{\beta\hbar\omega_0}{2}\right] - [1-\exp[-(N_0+1)\beta\hbar\omega_0]]\cosh\left[\frac{\beta\hbar\omega_0}{2}\right]\frac{\hbar\omega_0}{2}}{\sinh^2\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

$$= -\frac{M}{2\frac{1-\exp[-(N_0+1)\beta\hbar\omega_0]}{2\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]}}\frac{(N_0+1)\hbar\omega_0\exp[-(N_0+1)\beta\hbar\omega_0]\sinh\left[\frac{\beta\hbar\omega_0}{2}\right] - [1-\exp[-(N_0+1)\beta\hbar\omega_0]]\cosh\left[\right.}{\sinh^2\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

$$= -\frac{M\hbar\omega_0}{1-\exp[-(N_0+1)\beta\hbar\omega_0]}\frac{(N_0+1)\exp[-(N_0+1)\beta\hbar\omega_0]\sinh\left[\frac{\beta\hbar\omega_0}{2}\right] - [1-\exp[-(N_0+1)\beta\hbar\omega_0]]co}{\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

$$= M\frac{\hbar\omega_0}{2}\left[\coth\left[\frac{\beta\hbar\omega_0}{2}\right] - 2\frac{(N_0+1)\exp[-(N_0+1)\beta\hbar\omega_0]}{1-\exp[-(N_0+1)\beta\hbar\omega_0]}\right]$$

$$= M\hbar\omega_0\left[\frac{1}{2}\coth\left[\frac{\beta\hbar\omega_0}{2}\right] + \frac{(N_0+1)}{1-\exp[(N_0+1)\beta\hbar\omega_0]}\right]$$

and for $\beta\to 0$ I obtain

$$\langle E\rangle = M\hbar\omega_0\left[\frac{1}{\beta\hbar\omega_0} + \frac{(N_0+1)}{1-\left[1+(N_0+1)\beta\hbar\omega_0+\frac{1}{2}(N_0+1)^2(\beta\hbar\omega_0)^2\right]}\right]$$

$$= M\hbar\omega_0\left[\frac{1}{\beta\hbar\omega_0} + \frac{(N_0+1)}{1-1-(N_0+1)\beta\hbar\omega_0-\frac{1}{2}(N_0+1)^2(\beta\hbar\omega_0)^2}\right]$$

$$= M\hbar\omega_0\frac{1}{\beta\hbar\omega_0}\left[1 - \frac{1}{1+\frac{1}{2}(N_0+1)\beta\hbar\omega_0}\right]$$

$$= M\hbar\omega_0\frac{1}{2}(N_0+1)$$

d) $N_0 = \infty$

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial}{\partial T} M k_B T = M k_B$$

$N_0 < \infty$

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = 0$$

For $N_0 = \infty$ the number of quanta one can excite is not bounded, and one can therefore increase the energy of the system with increasing temperature. For $N_0 < \infty$ this is not possible, hence there is an upper bound for the energy stored in the system, and hence C_V has to go to zero for $T \rightarrow \infty$

Problem 5

Consider a monoatomic ideal gas.
a) What is the internal energy and the equation of state of an ideal gas?
b) Compute the entropy of an ideal gas as a function of T and V for constant particle number N starting from

$$dU = TdS - pdV$$

c) Compute the chemical potential of the ideal gas as a function of p and T starting from the Gibbs-Duhem relation

$$SdT - Vdp + Nd\mu = 0$$

Solutions:

a) What is the internal energy and the equation of state of an ideal gas?

$$U = \frac{3}{2}Nk_BT; \qquad pV = Nk_BT$$

b) Compute the entropy of an ideal gas as a function of T and V for constant particle number N starting from

$$dU = TdS - pdV$$

We start from

$$dS = \frac{dU}{T} + \frac{p}{T}dV = \frac{3}{2}Nk_B\frac{dT}{T} + Nk_B\frac{dV}{V}$$

We can now integrate the above expression from a state with entropy S_0 at T_0 and V_0 to obtain

$$S(T,V) - S_0(T_0,V_0) = \frac{3}{2}Nk_B\ln\frac{T}{T_0} + Nk_B\ln\frac{V}{V_0} = Nk_B\ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\frac{V}{V_0}\right\}$$

c) Compute the chemical potential of the ideal gas as a function of p and T starting from the Gibbs-Duhem relation

$$SdT - Vdp + Nd\mu = 0$$

Thus

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dp$$

Using next

$$S(T,V) - S_0(T_0,V_0) = \frac{3}{2}Nk_B\ln\frac{T}{T_0} + Nk_B\ln\frac{V}{V_0}$$

$$= Nk_B\ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\frac{V}{V_0}\right\} = Nk_B\ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\frac{p_0}{p}\right\}$$

and

$$V = \frac{Nk_BT}{p}$$

I obtain

$$d\mu = -\left[\frac{1}{N}S_0(T_0, V_0) + k_B \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\frac{p_0}{p}\right\}\right]dT + k_B T\frac{dp}{p}$$

and by integrating

$$\mu(T,p) - \mu(T_0,p_0) = -\int_{T_0}^{T} dT\left[\frac{1}{N}S_0(T_0,V_0) + k_B\frac{5}{2}\ln\left\{\left(\frac{T}{T_0}\right)\frac{p_0}{p}\right\}\right] + k_B T\int_{p_0}^{p}\frac{dp}{p}$$

$$= -\left[\frac{T-T_0}{N}S_0(T_0,V_0) + \frac{5}{2}k_B[T\ln T - T - (T_0\ln T_0 - T_0) - (T-T_0)\ln T_0]\right] + k_B T\ln\left(\frac{p}{p_0}\right)$$

$$= -\frac{T-T_0}{N}S_0(T_0,V_0) - \frac{5}{2}k_B T\ln\frac{T}{T_0} + \frac{5}{2}k_B(T-T_0) + k_B T\ln\left(\frac{p}{p_0}\right)$$