Physics 621 Midterm Exam NAME ______________________

Problem 1.
The partition function for N atoms trapped in a 3-dimensional harmonic oscillator potential is

$$Z = \frac{1}{N!}\left(\frac{1}{\beta\hbar\omega}\right)^{3N}.$$

(A) Express the single-atom partition function as a 6-dimensional integral corresponding to the sum over quantum states. (Do not evaluate the integral.)

$$Z_1 = \int \frac{dx\,dy\,dz\,dp_x\,dp_y\,dp_z}{h^3}\, \exp\left(-\beta\left[\tfrac{1}{2}m(x^2+y^2+z^2) + \tfrac{1}{2m}(p_x^2+p_y^2+p_z^2)\right]\right)$$

(B) Determine $\ln Z$ in the thermodynamic limit.

$$\ln Z = 3N \ln(1/\beta\hbar\omega) - \ln N! \qquad \ln N! \approx N\ln N - N$$

$$\ln Z \simeq N\left[-3\ln(\beta\hbar\omega) - \ln N + 1\right]$$

(C) Determine each of the following thermodynamic variables in the thermodynamic limit. Express them as functions of N and the temperature T.

a) Helmholtz free energy

$$F = \frac{1}{\beta}\log Z = NkT\left[3\ln\frac{kT}{\hbar\omega} - \ln N + 1\right]$$

b) total energy

$$U = -\left(\frac{\partial}{\partial\beta}\log Z\right)_N = -\left(-\frac{3N}{\beta}\right) = 3NkT$$

c) entropy

$$F = U - ST, \quad S = \frac{U-F}{T} = Nk\left[-3\ln\frac{kT}{\hbar\omega} + \ln N\right]$$

d) chemical potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_T = kT\left[3\ln\frac{kT}{\hbar\omega} - \ln N + 1\right] + NkT\left[-1/N\right]$$

$$= kT\left[3\ln\frac{kT}{\hbar\omega} - \ln N\right]$$

Problem 2.

A particle in a gravitational potential has energy

$$E = \tfrac{1}{2}mv^2 + mgz,$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$ and z ranges from 0 to ∞. The particle is in thermal equilibrium with a reservoir of temperature T.

(A) Write down the (unnormalized) probability distribution for each of the following:

a) the velocity vector (v_x, v_y, v_z),

$$\exp\left(-\tfrac{1}{2}m(v_x^2+v_y^2+v_z^2)/kT\right)\, dv_x\, dv_y\, dv_z$$

b) the velocity v,

$$v^2 \exp\left(-\tfrac{1}{2}m v^2/kT\right) dv$$

c) the coordinate z. $\exp\left(-mgz/kT\right) dz$

(B) Use the equipartition theorem to determine the average value of v^2.

$$\left\langle \tfrac{1}{2}m(v_x^2+v_y^2+v_z^2)\right\rangle = 3\cdot \tfrac{1}{2}kT \qquad \langle v^2\rangle = \frac{3kT}{m}$$

(C) Express the average value of v^4 as a ratio of definite integrals.

$$v^4 = \frac{\int_0^\infty dv\, v^4 \exp(-mv^2/2kT)}{\int_0^\infty dv\, v^2 \exp(-mv^2/2kT)}$$

(D) Calculate the average value of z.

$$\langle z\rangle = \frac{\int_0^\infty dz\, z \exp(-mgz/kT)}{\int_0^\infty dz\, \exp(-mgz/kT)} = \frac{\left(\frac{kT}{mg}\right)^2 \int_0^\infty dt\, te^{-t}}{\left(\frac{kT}{mg}\right)\int_0^\infty dt\, e^{-t}} = \frac{kT}{mg}$$

Useful integral : $\int_0^\infty dt\, t^n e^{-t} = n!$

Problem 3.

The internal partition function for a diatomic molecule at temperature T is

$$Z_{\text{int}} = e^{\beta\varepsilon_{\text{diss}}} \times \frac{1}{1-e^{-\beta\varepsilon_{\text{vib}}}} \times \sum_{\ell}(2\ell+1)e^{-\beta\ell(\ell+1)\varepsilon_{\text{rot}}}$$

where $\varepsilon_{\text{diss}}$, ε_{vib}, and ε_{rot} are energy parameters.

(A) Express the vibrational partition function as an infinite sum over a vibrational quantum number.

$$Z_{vib} = \frac{1}{1-e^{-\beta\epsilon_{vib}}} = \sum_{n=0}^{\infty} e^{-\beta(n\epsilon_{vib})}$$

(B) Use the analytic expression for the vibrational partition function to deduce the average vibrational energy.

$$\langle E_{vib}\rangle = -\frac{\partial}{\partial\beta}\log Z_{vib} = \frac{\partial}{\partial\beta}\log\left(1-e^{-\beta\epsilon_{vib}}\right)$$
$$= \frac{1}{1-e^{-\beta\epsilon_{vib}}}\cdot\left(-e^{-\beta\epsilon_{vib}}\right)\left(-\epsilon_{vib}\right) = \frac{\epsilon_{vib}}{e^{\beta\epsilon_{vib}}-1}$$

(C) In the low temperature limit, only the first few terms in the rotational partition function are important. Write down the first two terms in the sum over ℓ for a diatomic molecule that consists of

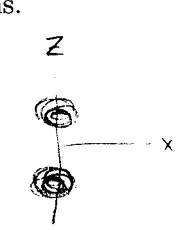
a) two distinct atoms,

$$\sum_{\ell=0}^{\infty}(2\ell+1)e^{-\beta\ell(\ell+1)\epsilon_{rot}} = 1 + 3e^{-2\beta\epsilon_{rot}} + \ldots$$

b) two identical atoms whose nuclei are spin-0 bosons.

$$\sum_{\substack{\ell=0 \\ \text{even}}}^{\infty}(2\ell+1)e^{-\beta\ell(\ell+1)\epsilon_{rot}} = 1 + 5e^{-6\beta\epsilon_{rot}} + \ldots$$

(D) Use the equipartition theorem to deduce the average rotational energy in the high-temperature limit for a diatomic molecule that consists of two distinct atoms. Identify the relevant quadratic degrees of freedom.



quadratic degrees of freedom:

angular velocity around x axis: ω_x

angular velocity around y axis: ω_y

(if z is the symmetry axis)

rotational energy: $E_{rot} = \frac{1}{2}I\left(\omega_x^2+\omega_y^2\right)$

average: $\langle E_{rot}\rangle = 2\cdot\frac{1}{2}kT = kT$

Problem 4.
Give the normalized probability distribution for microstates in each of the two following ensembles. (Define any new variable you introduce.)

M. microcanonical ensemble with total energy U

$$P_s = \frac{1}{\Omega(U)} \quad \text{if } U_s = U$$
$$= 0 \quad \text{if } U_s \neq U$$

$\Omega(U)$ = multiplicity of microstates with total energy U

C. canonical ensemble with temperature T

$$P_s = \frac{1}{Z} \exp(-\beta U_s) \qquad \beta = \frac{1}{T}$$

$$Z = \sum_s \exp(-\beta U_s)$$

The following three systems each consists of a gas with (an average of) N molecules and (an average) total energy U in a box of volume V, but they have different environments.
system 1: the box is surrounded by a vacuum chamber.
system 2: the box is inside a much larger box containing a gas of the same molecules.
system 3: the box is just a region of volume V with no walls
inside a much larger box containing a gas of the same molecules.

For each of the three systems 1, 2, and 3, what are the conserved quantities:
total energy "U" or number of molecules "N" or "both U and N" or "neither"?

system 1: U, N
system 2: N
system 3: neither

According to the Fundamental Assumption of Statistical Physics,
which of the ensembles ("M" or "C" or "both M and C" or "neither") describes accurately the equilibrium macroscopic behavior of the system for all values of N, U, and V?

system 1: M
system 2: C
system 3: neither

Which of the ensembles ("M" or "C" or "both M and C" or "neither") describes accurately the equilibrium macroscopic behavior of the system in the *thermodynamic limit* N, U, $V \to \infty$ with N/V, U/V fixed?

system 1: both M and C
system 2: both M and C
system 3: both M and C