

**You are graded on your work, with partial credit where it is deserved.**

**Please give clear, well-organized solutions.**

heat capacity (at constant volume) for liquid water =  $4200 \text{ J/kg} \cdot \text{K}$ ,  $0^\circ\text{C} = 273 \text{ K}$

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1. (a) (13) A kilogram of liquid water is heated from  $0^\circ\text{C}$  to  $100^\circ\text{C}$ . What is its change in entropy? (Note that the temperature is not constant.)

(b) (12) What is the change in the multiplicity (i.e., the number of allowed microstates)? Give the answer as the ratio  $W_{final} / W_{initial}$ .

2. Imagine an anomalous harmonic oscillator with frequency  $\nu$ , which has an upper limit  $N$  on the number of quanta that it can accommodate. I.e., the allowed states are  $n = 0, 1, 2, \dots, N$  with energies  $\epsilon_n = nh\nu$ , and  $N$  finite. (We are considering only the energy of the quanta, and leaving aside the zero-point energy.)

(a) (13) Show that the partition function can be summed in the form

$$Z = \frac{1 - e^{-(N+1)h\nu/kT}}{1 - e^{-h\nu/kT}}.$$

(b) (12) Calculate the approximate average energy  $\langle \epsilon \rangle$  at low temperatures ( $kT \ll h\nu$ ) in terms of  $kT$  and  $h\nu$ .

3. Let us treat each molecule in a gas as a hard sphere with volume  $v_0$ , so that the effective free volume per particle is reduced from  $v \equiv V / N$  to

$$v - v_0 = \frac{V - Nv_0}{N} .$$

Then the Sachur-Tetrode equation for the entropy  $S$  is modified to

$$S = Nk \ln \left( \frac{v - v_0}{\lambda_{th}^3} e^{5/2} \right) , \quad \lambda_{th} \equiv \frac{h}{(2\pi mkT)^{1/2}}$$

where  $N$  is the number of particles and  $T$  is the temperature.

(a) (5) For a general thermodynamic system, write  $dE$  in terms of  $dS$ ,  $dV$ ,  $dN$ , the temperature  $T$ , the pressure  $P$ , and the chemical potential  $\mu$ . Here  $E$  is the thermodynamic (or average) energy.

(b) (7) Then write  $dS$  in terms of  $dE$ ,  $dV$ , and  $dN$ , and show that

$$\left( \frac{\partial S}{\partial V} \right)_{E,N} = \frac{P}{T} .$$

(c) (8) One can show that  $E = E(T)$  -- i.e., the energy  $E$  is still a function of the temperature only. Using this fact, calculate the pressure  $P$  and show how the ideal gas equation of state is modified.

4. A single layer of xenon atoms is deposited on a graphite surface (in a low-temperature laboratory). Let us make the assumption that the atoms vibrate only in the 2 directions parallel to the surface, and that the graphite substrate can be ignored. Let us also treat the vibrations with a 2-dimensional Debye model, in which

$$\varepsilon = h\nu = c_s p$$

where  $\varepsilon = h\nu$  is a phonon energy,  $p = (p_x^2 + p_y^2)^{1/2}$  is the magnitude of a phonon momentum, and  $c_s$  is the speed of a vibrational wave.

(a) (5) Using periodic boundary conditions, with a periodicity length  $L$  (and area  $A = L^2$ ), show that the allowed values of the momentum components are  $p_x = \frac{h}{L}n_x$  and  $p_y = \frac{h}{L}n_y$ . (One way is to use the de Broglie relation between the wavelength  $\lambda_x$  and the momentum component  $p_x$ .)

(b) (5) In 2 dimensions, what is the approximate area in momentum space between  $p$  and  $p + \Delta p$ ? (Here  $\Delta p$  is small compared to  $p$ , but large compared to  $h/L$ . In 3 dimensions, we had the volume  $4\pi p^2 \Delta p$ .)

(c) (5) With 2 transverse polarizations, how many vibrational modes are there in  $\Delta p$  at  $p$ ?

(d) (5) Calculate the density of states  $D(\nu)$ , defined by  $D(\nu)\Delta\nu = \text{number of modes in } \Delta\nu \text{ at } \nu$ .

(e) (5) Assuming that the average number of phonons in the mode with frequency  $\nu$  is  $\bar{n}(\nu) = \frac{1}{e^{h\nu/kT} - 1}$ , write down the expression for the vibrational energy  $\langle E \rangle$  at temperature  $T$  as an integral over  $\nu$ , just calling the upper limit  $\nu_{\text{max}}$  (and not actually calculating it).

(f) (5) Show that the heat capacity at low temperatures is proportional to  $T^n$ , while at the same time determining  $n$ .