

# PC5202 Advanced Statistical Mechanics

## Assignment 1 (due Thursday 30 Jan 20)

*For assignments, handwritten or typed solutions, with sufficient details (steps), are required to hand in with the answers in hard copy on the due date during a class. Discussing of the problems are encouraged but solution must be worked out independently. In particular, copy/paste solution from the web is strongly discouraged. For tutorial problems, hand-in is not needed. But it will be good if you try to work them out first. Tutorials will be conducted using part of the lecture times.*

1. Given the equations of state of “simple ideal gas”  $PV = Nk_B T$  and  $U = (3/2)Nk_B T$ , where  $P$  is pressure,  $V$  is volume,  $T$  is temperature,  $k_B$  is the Boltzmann constant, determine ‘the fundamental relation’ - entropy  $S$  as a function of internal energy  $U$ , volume,  $V$ , number of particle  $N$ ,  $S(U, V, N)$ , using thermodynamic method.
2. Consider three variables  $x$ ,  $y$ , and  $z$  which are related functionally, i.e.,  $x=x(y,z)$ , or  $y=y(x,z)$ , or  $z=z(x,y)$ , show that  $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$ . Using this relation to show that the thermal expansion coefficient can be written in two alternative forms,  $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{B} \left(\frac{\partial P}{\partial T}\right)_v$ , where  $B$  is called bulk modulus. Work out the definition of bulk modulus  $B$ .
3. There is some controversy recently in the literature as whether absolute temperature  $T$  in Kelvin scale can be negative or not. Write in not more than half a page, the reason for and against negative absolute temperature. To answer this question properly, you need to do a literature search, read them, write a report, and cite the papers you have read.

## Tutorial 1 (do not hand in, we'll work some of this out in class)

**1.10-1.** (page 32 of Callen, 2<sup>nd</sup> ed, with some modification)

The following eleven equations are purported to be fundamental relations of various thermodynamic systems. However, five are inconsistent with one or more of postulates II, III, and IV and consequently are not physically acceptable; one of them violate concavity with respect to energy  $U$ , thus unstable (see page 204 of Callen). In each case qualitatively sketch a plot of the fundamental relationship between  $S$  and  $U$  (with  $N$  and  $V$  hold constant). Find the equations that are not physically permissible and indicate the postulates and conditions violated by each. [Focus on the  $U$  dependence only]

The quantities  $a$  and  $b$  are positive constants, and in all cases in which fractional exponents appears only the real positive root is to be taken.

- a)  $S = a (NVU)^{1/3}$
- b)  $S = a (NU/V)^{2/3}$
- c)  $S = a (NU + bV^2)^{1/2}$
- d)  $S = a V^3/(NU)$
- e)  $S = (N^2VU^2)^{1/5}$
- f)  $S = a N \ln (b UV/N^2)$
- g)  $S = a (NU)^{1/2} \exp(-bV^2/N^2)$
- h)  $S = a (NU)^{1/2} \exp(-bUV/N)$
- i)  $U = a S^2/V \exp(b S/N)$
- j)  $U = a N V (1 + b S/N) \exp(-b S/N)$
- k)  $S = a U^2/N + b (UN)^{1/2}$

**Example 1** (Callen, pages 51-52) Three cylinders of identical cross-sectional areas are fitted with pistons, and each contains a gaseous system (not necessarily of the same composition). The pistons are connected to a rigid bar hinged on a fixed fulcrum, as indicated in Fig.2.1 (see Callen, page 52). The “moment arms,” or the distances from the fulcrum, are in the ratio of 1:2:3. The cylinders rest on a heat conductive table of negligible mass; the table makes no contribution to the physics of the problem except to ensure that the three cylinders are in diathermal contact. The entire system is isolated and no pressure acts on the external surfaces of the pistons. Find the relation of pressures and of temperatures in the three cylinders.

**Conceptual questions:** (a) What is a quasi-static process? (b) What is a triple point? How is the Kelvin SI scale defined? (c) What is the definition of (electro-) chemical potential? (d) Why we need to postulate  $\partial S/\partial U \geq 0$ ? (e) Why we need  $\partial^2 S/\partial U^2 \leq 0$ ? (f) Under what conditions entropy increases? (g) State the basic/fundamental properties for temperature  $T$ . (h) State the fundamental properties of entropy  $S$ . (i) what is adiabatic wall, diathermal wall, semi-permeable wall, closed system, open system, isolated system?