## $IF/UFRJ \\ Statistical Mechanics - 2025/1 - Raimundo \\$

## Problem Set #8 – Approximation Methods 26/5/2024

- 1. Obtain the correction terms, to lowest order in the density, for the following quantities:<sup>1</sup> Gibbs free energy, entropy, internal energy, and specific heat at constant volume. Express your results in terms of the noninteracting quantities (i.e.,  $G^{(0)}$ ,  $S^{(0)}$ , and so forth), and of  $B_2(T)$  and its derivatives.
- 2. Obtain the third order (in the density) virial coefficient,  $B_3(T)$ , in the expansion of  $P/k_BT$ . Express it in terms of the  $J_n$  integrals defined in §7.2.2 of the LN.
- 3. The molecules of a gas interact according to a two-body potential, u(r). Obtain the corrections to ideal gas behaviour for the Helmholtz and Gibbs free energies, for the equation of state, entropy, internal energy, and specific heats (at constant volume and constant pressure), in the following cases:

(a) 
$$u(r) = \alpha/r^n, \ n > 0, \tag{1}$$

where  $\alpha$  is a constant.

(b) 
$$u(r) = \begin{cases} \infty & \text{if } r < a \\ -u_0 & \text{if } a < r < b \\ 0 & \text{if } r > b, \end{cases}$$
 (2)

where  $u_0$ , a and b are constants.

Discuss your results!

<sup>&</sup>lt;sup>1</sup>The correction to the Helmholtz free energy was derived in §7.2 of the LN.