Problem set 13

Due June 9, 2026

1. Given the equation of state of the grand canonical system

$$pV = k_B T \ln \Xi$$

and the expansion of the grand partition function Ξ in terms of Z_N's

$$\Xi = 1 + \sum_{N=1}^{\infty} \frac{Z_N(V,T)}{N!} z^N$$

with

$$z = \lambda Q_1 / V$$

$$Z_N = N! \left(\frac{V}{Q_1}\right)^N Q_N = \int \cdots \int \exp\left(-U_N / k_B T\right) d\mathbf{r}_1 \ldots d\mathbf{r}_N$$

where λ is the fugacity, Q_N is the partition function of a canonical system with N particles, U_N is the interaction energy for an N-particle system, **derive the expressions for the first 2 coefficients, b_1 and b_2, in the expansion of pressure in terms of z.**

$$p = k_B T \sum_{j=1}^{\infty} b_j z^j$$

2. Sketch the cluster diagrams corresponding to the following products of the f-functions in the expansion of pressure in terms of density.

$$f_{12} f_{23} f_{34} f_{45} f_{51} f_{14} f_{25}$$
$$f_{12} f_{23} f_{13} f_{34} f_{45} f_{46} f_{56}$$

3. Given the experimental data of the temperature dependence of the second virial coefficient of gaseous argon that can be found in the US

National Bureau of Standards report, Sengers JMH, Klein M, and Gallagher JS (1971). Pressure-volume-temperature relationships of gases virial coefficients. Defense Technical Information Center, Fort Belvoir, USA, `https://apps.dtic.mil/sti/pdfs/AD0719749.pdf` (a copy of the respective page attached to the printed version of this Problem set), determine the three parameters of the square-well potential: ϵ, σ, and λ of the square-well potential of this element. The second-order virial coefficient for the square-well potential is expressed as follows:

$$B_2(T) = \frac{2\pi\sigma^3}{3}\left[1 - \left(\lambda^3 - 1\right)\left(e^{\frac{\epsilon}{RT}} - 1\right)\right]$$

The following is not obligatory but recommended to solve. Try to determine the parameters of the Lennard-Jones potential (note that the latter will require numerical integration). The formula is as follows:

$$B_2(T) = -\frac{1}{2}\int\limits_0^\infty \left[\exp\left\{-\frac{4\epsilon}{RT}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]\right\} - 1\right] 4\pi r^2 dr$$

Compare the results with those in table 12.3 of Sherwood and Prausnitz, *J. Chem. Phys.*, **41**, 421 (1964) included in the lecture slides.