Problem set 14

Due June 16, 2026

1. Based on the expression of pressure in terms of pair-correlation function (under the assumption that the interaction energy is pairwise-additive), which is termed the pressure equation

$$\frac{p}{k_B T} = \rho - \frac{\rho^2}{6k_B T}\int_0^\infty r u'(r) g(r) 4\pi r^2 dr$$

where ρ is the particle number density, g is the radial pair-correlation function, $u(r)$ is the particle-particle potential energy of interactions, r is the particle-particle distance, T is the absolute temperature and k_B is the Boltzmann constant, and the expansion of the radial pair-correlation function, g, in density, ρ,

$$g(r,\rho,T) = g_\circ(r,T) + \rho g_1(r,T) + \rho^2 g_2(r,T)$$

demonstrate that the second virial coefficient of the pressure expansion in density obtained from inserting the density expansion of g into the pressure equation is equal to that obtained from the theory of imperfect gases

$$B_2(T) = -2\pi\int_0^\infty \left[\exp\left(-\frac{u(r)}{k_B T}\right) - 1\right] r^2 dr$$

provided that

$$g_\circ(r,T) = \exp\left(-\frac{u(r)}{k_B T}\right)$$

Hint: Apply the *per-partes* formula to the integral in the expression for $B_2(T)$, selecting $\exp\left(-\frac{u(r)}{k_B T}\right) - 1$ as the first function under the integral and r^2 as the first derivative of the second one.