DS 12:
Mean Field Theories

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1 Deriving the van der Waals equation of state

(a) Begin by justifying the excluded volume term in the van der Waals equation of state.

(b) Next, we will introduce some interactions between the particles when these particles are far apart. Let us consider a *pair-wise* interaction, described by some potential energy $\phi(r)$, where r is the distance between the particles in question. Show that the total potential energy for *one* molecule due to these interactions is given by

$$\delta u = \int_0^\infty \phi(r) \times n(r) \times 4\pi r^2 \mathrm{d}r, \tag{1}$$

where $n(r)$ is the number of particles per unit volume that are a distance r away from the particle in question.

(c) Since we are considering an attractive interaction, introduce an energy per interacting *pair*m given by

$$\epsilon \equiv \frac{1}{2}\int_0^\infty -\phi(r) \times 4\pi r^2 \mathrm{d}r. \tag{2}$$

(d) Now, if you assume that $n(r) \equiv \bar{n}$, in other words, the system is homogeneous so that the mean number of particles per unit volume is the same everywhere, show that you can write

$$\delta u \approx -2\bar{n}\epsilon. \tag{3}$$

(e) This is the potential energy of one single particle. Show that the total potential energy of all the particles is

$$\delta U = -\frac{N^2\epsilon}{V}, \tag{4}$$

from which you can show that

$$U(T,V) = U_{\text{ideal}}(T) - \frac{N^2\epsilon}{V}. \tag{5}$$