Density fluctuations and compressibility [tln61]

Average number of particles in volume V:

$$\mathcal{N} = \langle N \rangle = \sum_{N=0}^{\infty} \frac{1}{ZC_N} \int_{\Gamma_N} d^{6N}X\, N e^{-\beta H_N(\mathbf{X})+\beta\mu N} = \frac{1}{Z\beta}\frac{\partial Z}{\partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln Z.$$

Fluctuations in particle number (in volume V):

$$\langle N^2\rangle - \langle N\rangle^2 = \frac{1}{Z\beta^2}\frac{\partial^2 Z}{\partial \mu^2} - \left[\frac{1}{Z\beta}\frac{\partial Z}{\partial \mu}\right]^2 = \frac{1}{\beta^2}\frac{\partial^2 \ln Z}{\partial \mu^2} = \frac{1}{\beta^2}\frac{\partial(\beta\langle N\rangle)}{\partial \mu} = k_BT\left(\frac{\partial \mathcal{N}}{\partial \mu}\right)_{TV}.$$

Here we use $Z = Z(\beta, V, \mu)$.

Gibbs-Duhem: $d\mu = \frac{V}{\mathcal{N}}\, dp - \frac{S}{\mathcal{N}}\, dT \;\Rightarrow\; \left(\frac{\partial \mu}{\partial(V/\mathcal{N})}\right)_T = \frac{V}{\mathcal{N}}\left(\frac{\partial p}{\partial(V/\mathcal{N})}\right)_T.$

For $V=$ const: $\frac{\partial}{\partial(V/\mathcal{N})} = \frac{\partial \mathcal{N}}{\partial(V/\mathcal{N})}\frac{\partial}{\partial \mathcal{N}} = -\frac{\mathcal{N}^2}{V}\frac{\partial}{\partial \mathcal{N}}.$

For $\mathcal{N}=$ const: $\frac{\partial}{\partial(V/\mathcal{N})} = \frac{\partial V}{\partial(V/\mathcal{N})}\frac{\partial}{\partial V} = \mathcal{N}\frac{\partial}{\partial V}.$

$$\Rightarrow\; -\frac{\mathcal{N}^2}{V}\left(\frac{\partial \mu}{\partial \mathcal{N}}\right)_{TV} = V\left(\frac{\partial p}{\partial V}\right)_{T\mathcal{N}} \quad\Rightarrow\quad \left(\frac{\partial \mu}{\partial \mathcal{N}}\right)_{TV} = \frac{V}{\mathcal{N}^2}\,\kappa_T^{-1}.$$

Compressibility: $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T\mathcal{N}}.$

Fluctuations in particle number: $\langle N^2\rangle - \langle N\rangle^2 = \frac{\mathcal{N}^2}{V}\, k_BT\kappa_T.$

An alternative expression for $\langle N^2\rangle - \langle N\rangle^2$ is calculated in exercise [tex95].

The density fluctuations for a classical ideal gas are calculated in exercise [tex96].

At the critical point of a liquid-gas transition, the isotherm has an inflection point with zero slope ($\partial p/\partial V = 0$), implying $\kappa_T \to \infty$. The strongly enhanced density fluctuations are responsible for critical opalescence.