S9.B. Ornstein-Zernicke Equation

Since n_2^N is a (conditional) probability distribution, it should satisfy [c.f. (5.21)]

$$n_2^N(\boldsymbol{q}_1, \boldsymbol{q}_2) = \int d\,\boldsymbol{q}_3\, n_2^N(\boldsymbol{q}_1, \boldsymbol{q}_3)\, n_2^N(\boldsymbol{q}_3, \boldsymbol{q}_2)$$

So does its dimensionless version g_2^N.

Although the same cannot be proved for $h = g_2^N - 1$, some semblance of the behavior is expected.

For short-range potentials, it is then reasonable to propose the existence of a basic, short-range part $C(q)$ on which an arbitrary $h(q)$ can be built. Mathematically, this means

$$h(q_{12}) = C(q_{12}) + \langle n\rangle \int d\,\boldsymbol{q}_3\, C(q_{13})\, h(q_{32}) \tag{9.81}$$

$$= C(q_{12}) + \langle n\rangle \int d\,\boldsymbol{q}_3\, C(q_{13})\, C(q_{32})$$

$$+\langle n\rangle^2 \int d\,\boldsymbol{q}_3 \int d\,\boldsymbol{q}_4\, C(q_{13})\, C(q_{34})\, h(q_{42})$$

and so on. (9.81) is known as the Ornstein-Zernicke equation. and $C(q)$, the direct correlation function.

Note that the factor $\langle n\rangle$ in the last term of (9.81) is necessary for keeping the term dimensionless like $h(q)$.

Introducing the Fourier transforms

$$h(\boldsymbol{q}) = \int \frac{d\,\boldsymbol{k}}{(2\pi)^3}\, e^{i\,\boldsymbol{k}\cdot\boldsymbol{q}}\, \tilde{h}(\boldsymbol{k}) \tag{9.82a}$$

$$C(\boldsymbol{q}) = \int \frac{d\,\boldsymbol{k}}{(2\pi)^3}\, e^{i\,\boldsymbol{k}\cdot\boldsymbol{q}}\, \tilde{C}(\boldsymbol{k}) \tag{9.82b}$$

(9.81) becomes

$$\int \frac{d\,\boldsymbol{k}}{(2\pi)^3}\, e^{i\,\boldsymbol{k}\cdot\boldsymbol{q}_{12}}\, \tilde{h}(\boldsymbol{k})$$

$$= \int \frac{d\,\boldsymbol{k}}{(2\pi)^3}\, e^{i\,\boldsymbol{k}\cdot\boldsymbol{q}_{12}}\, \tilde{C}(\boldsymbol{k}) + \langle n\rangle \int d\,\boldsymbol{q}_3 \int \frac{d\,\boldsymbol{k}}{(2\pi)^3} \int \frac{d\,\boldsymbol{k}'}{(2\pi)^3}\, e^{i\,\boldsymbol{k}\cdot\boldsymbol{q}_{13} + i\,\boldsymbol{k}'\cdot\boldsymbol{q}_{32}}\, \tilde{C}(\boldsymbol{k})\, \tilde{h}(\boldsymbol{k}')$$

Using

$$i\,\boldsymbol{k}\cdot\boldsymbol{q}_{13} + i\,\boldsymbol{k}'\cdot\boldsymbol{q}_{32} = i\,(\boldsymbol{k} - \boldsymbol{k}')\cdot\boldsymbol{q}_3 + i\,\boldsymbol{k}'\cdot\boldsymbol{q}_2 - i\,\boldsymbol{k}\cdot\boldsymbol{q}_1$$

the last term becomes

$$\langle n\rangle \int \frac{d\,\boldsymbol{k}}{(2\pi)^3} \int d\,\boldsymbol{k}'\, \delta(\boldsymbol{k} - \boldsymbol{k}')\, e^{i\,\boldsymbol{k}'\cdot\boldsymbol{q}_2 - i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, \tilde{C}(\boldsymbol{k})\, \tilde{h}(\boldsymbol{k}')$$

$$= \langle n\rangle \int \frac{d\,\boldsymbol{k}}{(2\pi)^3}\, e^{i\,\boldsymbol{k}\cdot\boldsymbol{q}_{12}}\, \tilde{C}(\boldsymbol{k})\, \tilde{h}(\boldsymbol{k})$$

so that

$$\tilde{h}(\boldsymbol{k}) = \tilde{C}(\boldsymbol{k}) + \langle n\rangle\, \tilde{C}(\boldsymbol{k})\, \tilde{h}(\boldsymbol{k}) \tag{9.83}$$

$$= \frac{\tilde{C}(\boldsymbol{k})}{1 - \langle n\rangle\, \tilde{C}(\boldsymbol{k})} \tag{9.83a}$$

Using the inverse transform

$$\tilde{h}(\boldsymbol{k}) = \int d\,\boldsymbol{q}\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}}\, h(\boldsymbol{q})$$

the compressibility equation (9.80) becomes

$$k_B T \left(\frac{\partial n}{\partial P} \right)_T = 1 + \langle n \rangle \tilde{h}(0) \tag{9.84}$$

$$\rightarrow \quad \frac{1}{k_B T} \left(\frac{\partial P}{\partial n} \right)_T = \frac{1}{1 + \langle n \rangle \tilde{h}(0)} = \frac{1}{1 + \langle n \rangle \frac{\tilde{C}(0)}{1 - \langle n \rangle \tilde{C}(0)}} = 1 - \langle n \rangle \tilde{C}(0)$$

$$= 1 - \langle n \rangle \int d\boldsymbol{q}\, C(\boldsymbol{q}) \tag{9.85}$$

$C(q)$ obtained from molecular dynamics using the Lennard-Jones potential is shown in Reichl's Fig.9.7. Comparison between the resultant structural factor $S(k)$ and experiment is shown in Fig.9.6.

In general, the Ornstein-Zernicke equation must be solved numerically.

Percus and Yevick proposed the ansatz

$$C(q) = g(q) \left(1 - e^{\beta \mathcal{V}(q)} \right) \tag{9.86}$$

so that (9.81) becomes

$$h(q_{12}) = g(q_{12}) \left(1 - e^{\beta \mathcal{V}(q_{12})} \right) + \langle n \rangle \int d\boldsymbol{q}_3\, g(q_{13}) \left(1 - e^{\beta \mathcal{V}(q_{13})} \right) h(q_{32})$$

$$0 = 1 - g(q_{12})\, e^{\beta \mathcal{V}(q_{12})} + \langle n \rangle \int d\boldsymbol{q}_3\, g(q_{13}) \left(1 - e^{\beta \mathcal{V}(q_{13})} \right) h(q_{32})$$

$$\rightarrow \quad g(q_{12}) = e^{-\beta \mathcal{V}(q_{12})} + \langle n \rangle e^{-\beta \mathcal{V}(q_{12})} \int d\boldsymbol{q}_3\, g(q_{13}) \left(1 - e^{\beta \mathcal{V}(q_{13})} \right) h(q_{32}) \tag{9.87}$$

which is known as the Percus-Yevick equation and can be solved analytically for the hard sphere potential.

Isotherms of the equation of state of argon calculated using the P-Y equation for the Lennard-Jones potential are shown in Reichl's Fig.9.8. Interestingly, the P-Y equation has no real solution in a large region in the diagram. This region breaks an isotherm that may have gone through it into two branches in the manner of the coexistence region between the liquid and gas phases.

Wertheim and Thiele solved the P-Y equation analytically for the hard sphere potential. Putting the solution into the pressure equation (9.72), Thiele obtained an equation of state

$$P = \frac{\langle N \rangle}{V} k_B T \, \frac{1 + 2x + 3x^2}{(1-x)^2} \tag{9.88}$$

Putting the solution into the compressibility equation, he got

$$P = \frac{\langle N \rangle}{V} k_B T \, \frac{1 + x + x^2}{(1-x)^3} \tag{9.89}$$

where [see §9.C.3]

$$x = \frac{\frac{1}{4} \langle N \rangle b_0}{V} = \frac{1}{4} n\, b_0 \qquad\qquad b_0 = \frac{2}{3} \pi \sigma^3$$

Note that the difference between (9.88) & (9.89) is of order x^3 :

In[1]:= $\frac{1 + 2x + 3x^2}{(1-x)^2} - \frac{1 + x + x^2}{(1-x)^3} + O[x]^6$

Out[1]= $-3x^3 - 9x^4 - 18x^5 + O[x]^6$

This discrepancy arises because the O-Z equation is not exact.

Note that both (9.88) & (9.89) are undefined for $x = 1$, which is much greater than the close-packed density

$$x_{\text{cp}} = \frac{\frac{1}{4}\langle N\rangle b_0}{V_{\text{cp}}} = \frac{\frac{1}{4}\langle N\rangle b_0}{\frac{3\sqrt{2}}{4\pi}\langle N\rangle b_0} = \frac{\pi}{3\sqrt{2}} \approx 0.74$$