Statistical Mechanics of Liquids

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3.5.1   Distribution Functions

The density expansions of distribution functions can be done in a similar way as the virial expansion. We work in the grand canonical ensemble, and start with the definition of the two-body distribution function:

$$\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\Xi} \sum_{N=2}^{\infty} \frac{z^N}{(N-2)!} \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N e^{-\beta U_N(\boldsymbol{r}^N)} \tag{3.1}$$

$$= \frac{1}{\Xi} \left[z^2 e^{-\beta u(r_{1,2})} + \sum_{N=2}^{\infty} \frac{z^N}{(N-2)!} \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N e^{-\beta U_N(\boldsymbol{r}^N)} \right], \tag{3.2}$$

$$= \frac{z^2 e^{-\beta u(r_{1,2})}}{\Xi} \left[1 + \sum_{N=2}^{\infty} \frac{z^{N-2}}{(N-2)!} \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N e^{-\beta U_N'(\boldsymbol{r}^N)} \right], \tag{3.3}$$

where I assumed a pairwise additive interaction potential, and defined $U_N'(\boldsymbol{r}_3, .., \boldsymbol{r}_N) = -u(\boldsymbol{r}_{1,2}) + \sum_{i<j}^{N} u(\boldsymbol{r}_{i,j})$. Note that the activity, z, can be expanded in the density (see REF) $z = \rho - 2b_2\rho^2 + (8b_2^2 - 3b_3)\rho^3 + ...$ For a density expansion up to $\mathcal{O}(\rho^n)$, one needs to consider terms up to $\mathcal{O}(z^n)$. So, the term in the square bracktets already has a form of a density expansion. One only has to expand the inverse of the partition function in the activity, put in the density expansion of the activity and reorder the result in powers of density.

From the discussion on the virial expansion we know that

$$\Xi = 1 + \sum_{N=1}^{\infty} \frac{z^N}{N!} Z_N, \tag{3.4}$$

where Z_N is the configurational integral. This also gives the expansion of the inverse of the partition function:

$$\frac{1}{\Xi} = 1 - \sum_{N=1}^{\infty} \frac{z^N}{N!} Z_N + \left(\sum_{N=1}^{\infty} \frac{z^N}{N!} Z_N \right)^2 + \cdots \tag{3.5}$$

$$= 1 - \left(z Z_1 + \frac{1}{2} z^2 Z_2 + \cdots \right) + \left(z Z_1 + \frac{1}{2} z^2 Z_2 + \cdots \right)^2 + \cdots \tag{3.6}$$

$$= 1 - z Z_1 - \frac{1}{2} z^2 Z_2 + z^2 Z_1^2 + \mathcal{O}(z^3) \tag{3.7}$$

$$= 1 - z Z_1 - \frac{1}{2} z^2 \left(Z_2 - 2 Z_1^2 \right) + \mathcal{O}(z^3). \tag{3.8}$$

Using this expression for the inverse of the partition function in Eq. (3.3) gives

$$\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = z^2 e^{-\beta u(\boldsymbol{r}_{1,2})} \underbrace{[1 - z Z_1]}_{1/\Xi} \underbrace{\left[1 + z \int d\boldsymbol{r}_3 e^{-\beta U_3'(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)} \right]}_{\text{square bracktet in Eq. (3.3)}} + \mathcal{O}(z^4) \tag{3.9}$$

$$= z^2 e^{-\beta u(\boldsymbol{r}_{1,2})} \left\{ 1 - z \left[Z_1 - \int d\boldsymbol{r}_3 e^{-\beta U_3'(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)} \right] \right\} + \mathcal{O}(z^4). \tag{3.10}$$

The expansion of z is $z = \rho - 2 b_2 \rho^2 + \mathcal{O}(\rho^3)$ with $b_2 = \frac{1}{2V}(Z_2 - Z_1^2)$ (see REF). The expansion of z^2 is therefor $z^2 = \rho^2 - 4 b_2 \rho^3 + \mathcal{O}(\rho^4)$. Replacing z and z^2 in Eq. (3.10) gives

$$\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \underbrace{\left[\rho^2 - 4 b_2 \rho^3 \right]}_{z^2} e^{-\beta u(\boldsymbol{r}_{1,2})} \left\{ 1 - \underbrace{\rho}_{z} \left[Z_1 - \int d\boldsymbol{r}_3 e^{-\beta U_3'(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)} \right] \right\} + \mathcal{O}(z^4) \tag{3.11}$$

$$= e^{-\beta u(\boldsymbol{r}_{1,2})} \left[\rho^2 - \rho^3 \left(4 b_2 + Z_1 - \int d\boldsymbol{r}_3 e^{-\beta U_3'(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)} \right) \right] + \mathcal{O}(z^4). \tag{3.12}$$

Next we need to find an expression for the coefficient of the ρ^3 term. They were already evaluated when we discussed the virial expansion, but I will show it here again. For $4 b_2 = \frac{2}{V} \left(Z_2 - Z_1^2 \right)$ (See REF) we need to know Z_1 and Z_2. First Z_2, this is, by definition,

$$\frac{2}{V} Z_2 = \frac{2}{V} \int d\boldsymbol{r}_1' \int d\boldsymbol{r}_2' e^{-\beta u(|\boldsymbol{r}_1' - \boldsymbol{r}_2'|)} \tag{3.13}$$

$$= 2 \int d\boldsymbol{r}_3 e^{-\beta u(|\boldsymbol{r}_1' - \boldsymbol{r}_3|)} \tag{3.14}$$

$$= 2 \int d\boldsymbol{r}_3 e^{-\beta u(|\boldsymbol{r}_2' - \boldsymbol{r}_3|)}. \tag{3.15}$$

To go from the first to the second line, I changed coordinates from $d\boldsymbol{r}_2'$ to $d\boldsymbol{r}_3$ with $d\boldsymbol{r}_3 = d\boldsymbol{r}_1' - d\boldsymbol{r}_2'$, than the integrand is independent of $\boldsymbol{r}_1'$. So the $\boldsymbol{r}_1'$ integral gives a factor of V. Then shifting the origin of $\boldsymbol{r}_3$ to $\boldsymbol{r}_1'$ gives the second line, and shifting the origin to $\boldsymbol{r}_2'$ gives the third line. Shifting the origin is allowed because the system is homogeneous. Adding half of the second line to half of the third line gives

$$\frac{2}{V} Z_2 = \int d\boldsymbol{r}_3 e^{-\beta u(|\boldsymbol{r}_1 - \boldsymbol{r}_3|)} + e^{-\beta u(|\boldsymbol{r}_2 - \boldsymbol{r}_3|)}. \tag{3.16}$$

The configuration integral for one particle is equal to the volume which can be writen as $\int d\boldsymbol{r}_3$, so

$$\frac{2}{V}Z_1^2 = 2V \tag{3.17}$$

$$= 2\int d\boldsymbol{r}_3. \tag{3.18}$$

With the expression for $\frac{2}{V}Z_2$ and $\frac{2}{V}Z_1^2$ we have

$$\frac{2}{V}b_2 = \int d\boldsymbol{r}_3 e^{-\beta u(|\boldsymbol{r}_1-\boldsymbol{r}_3|)} + e^{-\beta u(|\boldsymbol{r}_2-\boldsymbol{r}_3|)} - 2 \tag{3.19}$$

$$= \int d\boldsymbol{r}_3 \left\{ f_{13} + f_{23} \right\}, \tag{3.20}$$

where in the last line I used the definition of the Mayer functions $f_{13} = e^{-\beta u(|\boldsymbol{r}_1-\boldsymbol{r}_3|)} - 1$, and similarly for f_{23}.

We can do the same kind of manipulations to the other part of the coefficient of ρ^3 in Eq. (3.12):

$$Z_1 - \int d\boldsymbol{r}_3 e^{-\beta U_3'(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3)} = -\int d\boldsymbol{r}_3 e^{-\beta u(|\boldsymbol{r}_1-\boldsymbol{r}_3|)} e^{-\beta u(|\boldsymbol{r}_1-\boldsymbol{r}_3|)} - 1 \tag{3.21}$$

$$= -\int d\boldsymbol{r}_3 \left(f_{13} + 1 \right) \left(f_{23} + 1 \right) - 1 \tag{3.22}$$

$$= -\int d\boldsymbol{r}_3 f_{13} + f_{23} + f_{13} f_{23}, \tag{3.23}$$

where I used the definition of U_3' and used $Z_1 = V = \int d\boldsymbol{r}_3$.

The coefficient of the ρ^3 term in Eq. (3.12) can now be expressed in terms of Mayer functions, and the density expansion can be writen as

$$\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = e^{-\beta u(r_{12})} \left[\rho^2 + \rho^3 \int d\boldsymbol{r}_3 f_{13} f_{23} \right] + \mathcal{O}(\rho^4). \tag{3.24}$$

One could, with considerably more effort, calculated the density expansion one order higher. This would result in

$$\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = e^{-\beta u(r_{12})} \left[\rho^2 + \rho^3 \int d\boldsymbol{r}_3 f_{13} f_{23} + \frac{1}{2}\rho^4 \int d\boldsymbol{r}_3 \int d\boldsymbol{r}_4 \big(2 f_{13} f_{34} f_{24} + \right.$$

$$\left. 4 f_{13} f_{34} f_{23} f_{24} + f_{13} f_{23} f_{14} f_{24} + f_{13} f_{23} f_{14} f_{24} f_{34} \big) \right] + \mathcal{O}(\rho^5). \tag{3.25}$$

3.5.2 Correlation Functions

4 Integral Equations for $g(r)$

TO DO: OUTLINE RHO(R1,R2;XI=0) = ...

4.1   The Kirkwood Equation

The goal of this section is to derive an integral equation for the pair-distribution function called the Kirkwood equation. The derivation shown here is based on Refs. [1] (section 32) and [2] (chapter 13-4).

For this, one can use a system with two kinds of particles, just as the system that was used to express the chemical potential using the pair-distribution function. ADD EQ. REF In this system the interaction potential of particle 1 with any of the other particles is scaled by ξ:

$$U_N(\boldsymbol{r}_1, .., \boldsymbol{r}_N) = \sum_{j=2}^{N} \xi u(\boldsymbol{r}_1, \boldsymbol{r}_j) + \sum_{\substack{i=2 \\ j>i}}^{N} u(\boldsymbol{r}_i, \boldsymbol{r}_j), \tag{4.1}$$

with $0 \leq \xi \leq 1$, so when $\xi = 1$ it is a system of N identical interacting particles, and when $\xi = 0$ it is a system consisting of one ideal particle and $N-1$ interacting particles. Because there are two species of particles in this system (particle 1 and the "normal" particles), this means that one can define two kinds of radial distribution functions: one for the distribution of the normal particles around particle 1, one for the distribution of the normale particles around an other normal particle. In these notes, the difference between these two functions is indicated by the arguments. When $\boldsymbol{r}_1$ is one of the arguments (or $|\boldsymbol{r}_1 - \boldsymbol{r}_j|$ with $j > 2$), it is the first kind; otherwise it is the second kind. When which distribution function is which is not clear from the arguments, I indicate the distribution function of the normal particles around particle 1 with $g_{(1,n)}^{(n)}(...)$ and the other kind with $g_{(n,n)}^{(n)}(...)$.

The starting point is the identity

$$kT \, ln \left(\rho^{(n)}(\boldsymbol{r}_1, .., \boldsymbol{r}_n; \xi) \right) = kT \, ln \left(\rho^{(n)}(\boldsymbol{r}_1, .., \boldsymbol{r}_n; \xi = 0) \right) +$$
$$\int_0^\xi d\xi' \frac{\partial}{\partial \xi'} kT \, ln \left(\rho^{(n)}(\boldsymbol{r}_1, .., \boldsymbol{r}_n; \xi') \right). \tag{4.2}$$

First we calculate

$$kT \frac{\partial}{\partial \xi} \rho^{(n)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_n; \xi) = kT \left(\frac{\partial}{\partial \xi} \frac{1}{Z_N(\xi)} \right) \frac{N!}{(N-n)!} \int d\boldsymbol{r}_{n+1} \cdots \int d\boldsymbol{r}_N e^{-\beta U_N(\xi)}$$
$$+ kT \frac{1}{Z_N(\xi)} \frac{N!}{(N-n)!} \int d\boldsymbol{r}_{n+1} \cdots \int d\boldsymbol{r}_N \frac{\partial}{\partial \xi} e^{-\beta U_N(\xi)}$$
$$= -kT \rho^{(n)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_n; \xi) \frac{1}{Z_N(\xi)} \frac{\partial}{\partial \xi} Z_N(\xi)$$
$$- \frac{N!}{(N-n)!} \frac{1}{Z_N(\xi)} \int d\boldsymbol{r}_{n+1} \cdots \int \boldsymbol{r}_N e^{-\beta U_N} \sum_{j=2}^{N} u(\boldsymbol{r}_1, \boldsymbol{r}_j).$$

The terms in the sum with $j < n + 1$ can be taken out of the integral:

$$kT\frac{\partial}{\partial\xi}\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi) = -kT\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi)\frac{1}{Z_N(\xi)}\frac{\partial}{\partial\xi}Z_N(\xi)$$

$$-\sum_{j=2}^{n}u(\boldsymbol{r}_1,\boldsymbol{r}_j)\underbrace{\frac{N!}{(N-n)!}\frac{1}{Z_N(\xi)}\int d\boldsymbol{r}_{n+1}\cdots\int \boldsymbol{r}_N e^{-\beta U_N}}_{=\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi)}$$

$$-\frac{N!}{(N-n)!}\frac{1}{Z_N(\xi)}\int d\boldsymbol{r}_{n+1}\cdots\int \boldsymbol{r}_N e^{-\beta U_N}\sum_{j=n+1}^{N}u(\boldsymbol{r}_1,\boldsymbol{r}_j).$$

$$(4.3)$$

Each term in the last sum in the contribute the same. So you can pick one, say $j = n+1$, and multiply by the number of terms in the sum, which is $N - n$. And we also need

$$-kT\frac{1}{Z_N(\xi)}\frac{\partial}{\partial\xi}Z_N(\xi) = \frac{1}{Z_N(\xi)}\int \boldsymbol{r}_1\cdots\int \boldsymbol{r}_N e^{-\beta U_N(\xi)}\sum_{j=2}^{N}u(\boldsymbol{r}_1,\boldsymbol{r}_j).$$

And again each term in the sum contributes the same, so you can pick the term with $j = 2$ and multiply by $N - 1$. So Eq. (4.3) becomes

$$kT\frac{\partial}{\partial\xi}\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi) = \rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi)\int d\boldsymbol{r}'_1\int d\boldsymbol{r}'_2 u(\boldsymbol{r}'_1,\boldsymbol{r}'_2)\underbrace{\frac{N-1}{Z_N(\xi)}\int d\boldsymbol{r}_3\cdots\int d\boldsymbol{r}_N e^{-\beta U_N}}_{=\frac{1}{N}\rho^{(1)}(\boldsymbol{r}'_1,\boldsymbol{r}'_2;\xi)}$$

$$-\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi)\sum_{j=2}^{n}u(\boldsymbol{r}_1,\boldsymbol{r}_j)$$

$$-\int d\boldsymbol{r}'_{n+1}u(\boldsymbol{r}_1,\boldsymbol{r}'_{n+1})\underbrace{\frac{N!}{(N-n)!}\frac{1}{Z_N(\xi)}\int d\boldsymbol{r}'_{n+2}\cdots\int \boldsymbol{r}_N e^{-\beta U_N}}_{=\rho^{(n+1)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}'_{n+1};\xi)}.$$

For Eq. (4.2) we need the derivative of the ln of $\rho^{(n)}$, which is the same as the previous equation devided by $\rho^{(n)}$.

$$kT\frac{\partial}{\partial\xi}ln\left(\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi)\right) = -\sum_{j=2}^{n}u(\boldsymbol{r}_1,\boldsymbol{r}_j) - \int d\boldsymbol{r}'_{n+1}u(\boldsymbol{r}_1,\boldsymbol{r}'_{n+1})\frac{\rho^{(n+1)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}'_{n+1};\xi)}{\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi)}$$

$$-\frac{1}{N}\int d\boldsymbol{r}'_1\int d\boldsymbol{r}'_2 u(\boldsymbol{r}'_1,\boldsymbol{r}'_2)\rho^{(1)}(\boldsymbol{r}'_1,\boldsymbol{r}'_2;\xi).$$

With this Eq. (4.2) becomes

$$kTln\left(\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi)\right) = kTln\left(\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi=0)\right) - \xi\sum_{j=2}^{n}u(\boldsymbol{r}_1,\boldsymbol{r}_j)$$

$$-\int_0^{\xi}d\xi'\int d\boldsymbol{r}'_{n+1}u(\boldsymbol{r}_1,\boldsymbol{r}'_{n+1})\frac{\rho^{(n+1)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}'_{n+1};\xi')}{\rho^{(n)}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_n;\xi')}$$

$$-\int_0^{\xi}d\xi'\frac{1}{N}\int d\boldsymbol{r}'_1\int d\boldsymbol{r}'_2 u(\boldsymbol{r}'_1,\boldsymbol{r}'_2)\rho^{(1)}(\boldsymbol{r}'_1,\boldsymbol{r}'_2;\xi').$$

The n-body density eveluated at $\xi = 0$ is

$$\rho^{(n)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_n; \xi = 0) = \frac{N!}{(N-n)!} \frac{1}{Z_N(\xi = 0)} \int d\boldsymbol{r}_{n+1} \cdots \int d\boldsymbol{r}_N e^{-\beta U_N(\xi = 0)}.$$

n configurational integral with $\xi = 0$ is the configurational integral of $N - 1$ particles times the volume (see ...), and $U_N(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N; \xi = 0) = U_{N-1}(\boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$, so

$$\rho^{(n)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_n; \xi = 0) = \frac{N!}{(N-n)!} \frac{1}{Z_N(\xi = 0)} \int d\boldsymbol{r}_{n+1} \cdots \int d\boldsymbol{r}_N e^{-\beta U_N(\xi = 0)}.$$

4.1.1 interpretation with potential of mean force

OLD STUFF FOR N=2

All that is to be done is to work out what the derivative on the right hand side is. For simplicity, I will do the $n = 2$ case here, and show the general case in App. . We need the derivative with respect of ξ of

$$\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi) = \frac{N(N-1)}{Z_N(\xi)} \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N \ e^{-\beta U_N(\xi)}. \tag{4.4}$$

This is

$$kT \frac{\rho^{(2)}(\partial \boldsymbol{r}_1, \boldsymbol{r}_2; \xi)}{\partial \xi} = \frac{N(N-1)}{Z_N(\xi)} \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N \ e^{-\beta U_N(\xi)}. \tag{4.5}$$

$$= \underbrace{kTN(N-1) \left(\frac{\partial}{\partial \xi} \frac{1}{Z_N(\xi)} \right) \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N \ e^{-\beta U_N(\xi)}}_{\equiv I_1}$$

$$+ \underbrace{kT \frac{N(N-1)}{Z_N(\xi)} \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N \ \frac{\partial}{\partial \xi} e^{-\beta U_N(\xi)}}_{\equiv I_2}. \tag{4.6}$$

The first integral is

$$I_1 = -\frac{kTN(N-1)}{Z_n(\xi)^2} \left(\frac{\partial}{\partial \xi} \underbrace{\int d\boldsymbol{r}_1 \cdots \int d\boldsymbol{r}_N \ e^{-\beta U_N(\xi)}}_{Z_N(\xi)} \right) \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N \ e^{-\beta U_N(\xi)} \tag{4.7}$$

$$= \rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi) \frac{-kT}{Z_N(\xi)} \int d\boldsymbol{r}_1 \cdots \int d\boldsymbol{r}_N \ e^{-\beta U_N(\xi)} \frac{\partial}{\partial \xi} \left(-\beta U_N(\xi) \right). \tag{4.8}$$

The $-\beta$ cancels the $-kT$ in the fraction, and the derivative in the integral is $\partial_\xi U_N = \sum_{j=2}^{N} u(\boldsymbol{r}_1, \boldsymbol{r}_j)$ (see (4.1)). There are $N - 1$ terms in this sum. Each term has the same contribution because the $\boldsymbol{r}$'s are all integration parameters. Therefore, one can pick one of the terms in the sum, say $u(\boldsymbol{r}_1, \boldsymbol{r}_2)$, and multiply the result by $N - 1$. This results in

$$I_1 = \rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi) \frac{1}{N} \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 u(\boldsymbol{r}_1, \boldsymbol{r}_2) \frac{N(N-1)}{Z_N(\xi)} \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N \ e^{-\beta U_N(\xi)}, \tag{4.9}$$

where I multiplied and divided by N because the second fraction and the second set of integrals is $\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi)$. So the integral is

$$I_1 = \rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi) \frac{1}{N} \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 u(\boldsymbol{r}_1, \boldsymbol{r}_2) \rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi). \tag{4.10}$$

For the second integral in Eq. (4.5) we need

$$kT \frac{\partial}{\partial \xi} e^{-\beta U_N(\xi)} = -e^{-\beta U_N(\xi)} \frac{\partial}{\partial \xi} U_N \tag{4.11}$$

$$= -e^{-\beta U_N(\xi)} \sum_{j=2}^{N} u(\boldsymbol{r}_1, \boldsymbol{r}_j) \tag{4.12}$$

$$= -e^{-\beta U_N(\xi)} \left(u(\boldsymbol{r}_1, \boldsymbol{r}_2) + \sum_{j=3}^{N} u(\boldsymbol{r}_1, \boldsymbol{r}_j) \right). \tag{4.13}$$

The sum in the last line has $N - 2$ terms, so one can replace the sum by a single term, say $u(\boldsymbol{r}_1, \boldsymbol{r}_3)$, and multiply by the number of terms. This gives

$$I_2 = -u(\boldsymbol{r}_1, \boldsymbol{r}_2) \frac{N(N-1)}{Z_N(\xi)} \int d\boldsymbol{r}_3 \cdots \int d\boldsymbol{r}_N \ e^{-\beta U_N(\xi)} \tag{4.14}$$

$$- \frac{N(N-1)(N-2)}{Z_N(\xi)} \int d\boldsymbol{r}_3 u(\boldsymbol{r}_1, \boldsymbol{r}_3) \int d\boldsymbol{r}_4 \cdots \int d\boldsymbol{r}_N \ e^{-\beta U_N(\xi)} \tag{4.15}$$

$$= -u(\boldsymbol{r}_1, \boldsymbol{r}_2) \rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi) - \int d\boldsymbol{r}_3 u(\boldsymbol{r}_1, \boldsymbol{r}_3) \rho^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3; \xi). \tag{4.16}$$

From Eq. (4.2) with $n = 2$ we have

$$kT \ ln \left(\rho^{(n)}(\boldsymbol{r}_1, .., \boldsymbol{r}_n; \xi) \right) = kT \ ln \left(\rho^{(n)}(\boldsymbol{r}_1, .., \boldsymbol{r}_n; \xi = 0) \right) +$$

$$\int_0^\xi d\xi' \frac{\partial}{\partial \xi'} kT \ ln \left(\rho^{(n)}(\boldsymbol{r}_1, .., \boldsymbol{r}_n; \xi') \right) \tag{4.17}$$

$$= kTln(\rho^2) + \int_0^\xi d\xi' \frac{1}{\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi')} kT \frac{\partial}{\partial \xi} \rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi') \tag{4.18}$$

$$= kTln(\rho^2) + \int_0^\xi d\xi' \frac{1}{\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi')} (I_1 + I_2), \tag{4.19}$$

where to go from the first to the second line I used that $\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi = 0) = \rho^2 g^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi = 0) = \rho^2$ because if particle 1 does not interact with any of the other particles it is not correlated with any other particle. Replacing I_1 and I_2 with their explicit expressions results

in

$$kT \ln \left(\rho^{(n)}(\boldsymbol{r}_1, .., \boldsymbol{r}_n; \xi) \right) = kT ln(\rho^2) + \int_0^\xi d\xi' \bigg($$

$$\frac{1}{N} \int d\boldsymbol{r}_1' \int d\boldsymbol{r}_2' u(\boldsymbol{r}_1', \boldsymbol{r}_2') \rho^{(2)}(\boldsymbol{r}_1', \boldsymbol{r}_2'; \xi')$$

$$- u(\boldsymbol{r}_1, \boldsymbol{r}_2) - \int d\boldsymbol{r}_3 u(\boldsymbol{r}_1, \boldsymbol{r}_3) \frac{\rho^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3; \xi)}{\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi)} \bigg) \qquad (4.20)$$

$$= kT ln(\rho^2) - \xi u(\boldsymbol{r}_1, \boldsymbol{r}_2) +$$

$$\frac{1}{N} \int d\boldsymbol{r}_1' \int d\boldsymbol{r}_2' \int_0^\xi d\xi' u(\boldsymbol{r}_1', \boldsymbol{r}_2') \rho^{(2)}(\boldsymbol{r}_1', \boldsymbol{r}_2'; \xi') -$$

$$\int_0^\xi d\xi' u(\boldsymbol{r}_1, \boldsymbol{r}_3) \frac{\rho^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3; \xi')}{\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \xi')} \qquad (4.21)$$

4.2   The Born-Green-Yvon Equation

4.3   The Percus-Yevick Equation

4.4   Density Expansion of the Percus-Yevick Equation

4.5   Equations of State for Hard Spheres

4.5.1   Percus-Yevick

4.5.2   The Carnahan-Starling

5   Numerical Solutions

5.1   Numerical Solutions to Integral Equations

If the integral equation is not linear, it is probably not possible to solve it analytically and one needs te resort to numerical methods. The integral equations in this course have the form

$$f(r) = g(r) + \alpha \int dr' \ K[r, r'; f], \qquad (5.1)$$

where the function $g(r)$ and the kernel K are known and the goal is to find the function $f(r)$. The kernel depends on the function $f(r)$ and the parameters r and r'; for example, $K[r, r'; f] = g(r')^2 h(r - r')$, with h some other arbitrary function. Note that in this equation the functions $f(r)$, $g(r)$ and $h(r)$ are arbitrary and are not, nessecarily, the Mayer function, the pair-distribution function and the total-correlation function. The first step is to guess some acceptable form for the function $f(r)$, denoted by $f_0(r)$. One possibility is

$$f_0(r) = \lim_{\alpha \to 0} f(r) = g(r). \qquad (5.2)$$

The next step is to calculate an imporoved approximation to the function $f(r)$ by evaluating the right hand side of Eq. (5.1) with $f_0(r)$. Repeating this last step until the new approximation does not differ from the previous one, gives the final solution. So, the improved

solution is

$$f_{n+1}(r) = g(r) + \alpha \int dr' \ K[r, r'; f_n],\tag{5.3}$$

and the final solution is obtained when $f_{n+1}(r) \approx f_n(r)$. [1] In some cases one has a system of coupled equation. When this is the case, one has to solve multiple equations to get the improved solution.

The convergence of this method can be improved by mixing the old with the new solution:

$$f_{n+1}(r) = \eta f'_{n+1}(r) + (1 - \eta)f_n(r),\tag{5.4}$$

with $0 < \eta \leq 1$ and

$$f'_{n+1}(r) = g(r) + \alpha \int dr' \ K[r, r'; f_n].\tag{5.5}$$

As a convergence criteria one can use, for example,

$$\int dr \ \left(f'_{n+1}(r) - f_n(r)\right)^2 < \epsilon,\tag{5.6}$$

or

$$max_r \left\{|f'_{n+1}(r) - f_n(r)|\right\} < \epsilon,\tag{5.7}$$

for some ϵ.

5.2 PY + OZ in Fourier Space

In this section I will explain how to solve the PY + OZ in Fourier space. This is faster than the real space method.

I will first show the naive implimentation, and point out some of the problems with it, then solve the problems and show the final algorithm at the end of this section. The naive algorithm is:

1. Guess an acceptable initial $h(r)$ denoted by $h_0(r)$. For example, use the low-density solution $h_0(r) = \lim_{\rho \to 0} h(r)$ or use an $h(r)$ calculated for slightly different parameters.

2. Get the direct-correlation function $c_n(r)$ corresponding to $h_n(r)$ from the Percus-Yevick equation:

$$c_n(r) = f(r)e^{\beta u(r)} \left(h_n(r) - 1\right).\tag{5.8}$$

   For the first loop through the algorithm use $n = 0$.

3. Fourier Transform $c_n(r)$ to get $C_n(k)$.

---

[1] Of course, for the numerical evaluation of the integrals, they have to be approximated by a sum. For numerical algorithms for integration see for example [3].

4. Use the Ornstein-Zernike equation to the next Fourier transformed total-correlation function:

$$H_{n+1}(k) = \frac{C(k)}{1 - \rho C(k)}. \tag{5.9}$$

5. Fourier transform back to real space to get $h'_{n+1}(r)$.

6. Mix the new solution with the old one:

$$h_{n+1}(r) = \alpha h_n(r) + (1 - \alpha)h'_{n+1}(r), \tag{5.10}$$

with $0 \leq \alpha < 1$.

7. Check for convergence. If converged, you are done, else go to 2.

This algorithm will lead to multiplication and divisions by zeros and infinities. To avoid these, some alterations need to be made.

5.2.1 The Indirect Correlation Function

The Percus-Yevick Equation is

$$c(r) = f(r)y(r) \tag{5.11}$$

$$= \left[e^{-\beta u(r)} - 1\right] e^{\beta u(r)} \left[h(r) + 1\right] \tag{5.12}$$

$$= h(r) - \left[e^{\beta u(r)} h(r) + e^{\beta u(r)} - 1\right], \tag{5.13}$$

where I used $f(r) = e^{-\beta u(r)}$, $y(r) = e^{\beta u(r)}g(r)$ and $h(r) = g(r) - 1$ to go from the first to the second line. Both $c(r)$ and $h(r)$ are finite; therefor, the term in the square brackets is also finite. The exponentials in the square brackets diverge for potentials that are strongly repulsive at short distances, which is the case for the Lennard-Jones or Hard sphere potential. So there is some cancellation of infinities. This is not a problem for theoretical manipulation, but it makes numerical calculations impossible. Because the expression in the square brackets is finite, the problem is only in the representation of those terms. The problem can be solved by defining the indirect correlation function, $d(r)$ [2] , and work with the direct and indirect-correlation functions instead of the direct and the total-corelation functions.

The total-correlation function is the sum of the direct and the indirect-correlation function:

$$h(r) = c(r) + d(r). \tag{5.14}$$

The Percus-Yevick approximation, is an approximate relation between the direct and total-correlation function, but it can be rewriten, such that it is an approximate relation between the direct and indirect-correlation function:

$$c(r) = c(r) + d(r) - \left[e^{\beta u(r)}\left(c(r) + d(r)\right) + e^{\beta u(r)} - 1\right]. \tag{5.15}$$

---

[2]This is not a commonly used function and the symbol for this function is not used in other texts.

Reorder this to get:

$$e^{\beta u(r)}c(r) = d(r) - e^{\beta u(r)} + \left(1 - e^{\beta u(r)}\right) \tag{5.16}$$

$$= d(r)\left(1 - e^{\beta u(r)}\right) + \left(1 - e^{\beta u(r)}\right) \tag{5.17}$$

$$= (d(r) + 1)\left(e^{-\beta u(r)} - 1\right). \tag{5.18}$$

Multiplying both sides by $e^{-\beta u(r)}$ results in the Percus-Yevick approximation rewriten as a relation between the direct and indirect-correlation functions:

$$c(r) = f(r)\left(d(r) + 1\right). \tag{5.19}$$

The Mayer fucntion is finite everywhere, so this last equation can be used in numerical calculations.

The Ornstein-Zernike equation defines the relation between the direct and total-correlation function, but is can be rewriten to relate the direct to the indirect correlation function. The Fourier transform of the indirect-correlation function is

$$D(\boldsymbol{k}) = H(\boldsymbol{k}) - C(\boldsymbol{k}) \tag{5.20}$$

$$= \frac{C(\boldsymbol{k})}{1 - \rho C(\boldsymbol{k})} - C(\boldsymbol{k}), \tag{5.21}$$

where to I used the Ornstein-Zernike equation $\left(H(\boldsymbol{k}) = \frac{C(\boldsymbol{k})}{1 - \rho C(\boldsymbol{k})}\right)$ to go to the second line.

Equations (5.19) and (5.21) can be used to find a numerical solution for the direct and indirect correlation functions, and the sum of the two gives the total correlation function.

5.2.2 One More Change to the Naive Algorithm

The Fourier transformation of a isotropic function in $\mathbb{R}^3$ is (see App.C):

$$|\boldsymbol{k}|F(|\boldsymbol{k}|) = 4\pi \int_0^\infty dr \ |\boldsymbol{r}|f(|\boldsymbol{r}|)\sin(|\boldsymbol{k}||\boldsymbol{r}|), \tag{5.22}$$

and the inverse transformation is:

$$|\boldsymbol{r}|f(|\boldsymbol{r}|) = \frac{1}{2\pi^2} \int_0^\infty dk \ |\boldsymbol{k}|F(|\boldsymbol{k}|)\sin(|\boldsymbol{k}||\boldsymbol{r}|). \tag{5.23}$$

These definitions show that it is convenient to work with $|\boldsymbol{r}|f(|\boldsymbol{r}|)$ and $|\boldsymbol{k}|F(|\boldsymbol{k}|)$ in stead of $f(|\boldsymbol{r}|)$ and $F(|\boldsymbol{k}|)$, when one does these transformation repeatedly. It is therfore expedient to define the following four new functions:

$$\tilde{c}(r) = rc(r), \tag{5.24}$$

$$\tilde{d}(r) = rd(r), \tag{5.25}$$

$$\tilde{C}(k) = kC(k), \tag{5.26}$$

$$\tilde{D}(k) = kD(k), \tag{5.27}$$

and use these in the algorithm. The relations between $\tilde{c}(r)$ and $\tilde{C}(k)$, and $\tilde{d}(r)$ and $\tilde{D}(k)$ are

$$\tilde{C}(k) = 4\pi \int_0^\infty dr \ \tilde{c}(r) sin(kr), \ \tilde{c}(r) = \frac{1}{2\pi^2} \int_0^\infty dk \ \tilde{C}(k) sin(kr), \tag{5.28}$$

and

$$\tilde{D}(k) = 4\pi \int_0^\infty dr \ \tilde{d}(r) sin(kr), \ \tilde{d}(r) = \frac{1}{2\pi^2} \int_0^\infty dk \ \tilde{D}(k) sin(kr). \tag{5.29}$$

The Ornstein-Zernike equation for the functions $\tilde{C}(k)$ and $\tilde{D}(k)$ is

$$\tilde{D}(k) = \frac{\tilde{C}(k)}{1 - \rho\tilde{C}(k)/k} - \tilde{C}(k). \tag{5.30}$$

The division by k in the denominator on the right-hand side is not a problem because $\tilde{D}(0) = 0$ ($D(k)$ is finite, therfore $kD(k)|_{k=0} = 0$), so $k = 0$ need not be evaluated.

5.2.3 The Final Algorithm

The final version of the algorithm is similar in spirit to the naive one, but uses the transformed functions and the indirect-correlation function in stead of the total-correlation function.

1. Guess $\tilde{d}_0(r)$. For example, the low density solution, or the outcome of a previous calculation for different parameters.

2. Get $\tilde{c}_n(r)$ from the modified Percus-Yevick approximation (Eq. (5.19)). In the first loop through the algorithm $n = 0$.

3. Use Eq. (5.28) to get $\tilde{C}_n(k)$.

4. Use Eq. (5.30) to get $\tilde{D}'_{n+1}(k)$:

$$\tilde{D}'_{n+1}(k) = \frac{\tilde{C}_n(k)}{1 - \rho\tilde{C}_n(k)/k} - \tilde{C}_n(k). \tag{5.31}$$

5. Use (5.29) to get $\tilde{d}'_{n+1}(r)$.

6. Mix the new indirect-correlation function with the old one:

$$\tilde{d}_{n+1}(r) = \alpha\tilde{d}_n(r) + (1 - \alpha)\tilde{d}'_{n+1}, \tag{5.32}$$

with $0 \le \alpha < 1$.

7. Check for convergence. If converged, go to 8, else go to 2.

8. Calculate the total-correlation function from the direct and indirect-correlation functions:

$$h(r) = \begin{cases} -1, & \text{if } r = 0 \\ \tilde{c}_n(r)/r + \tilde{d}_n(r)/r, & \text{if } r > 0. \end{cases} \tag{5.33}$$

As a convergence critecion one can use, for example,

$$\int dr \, \left[\tilde{d}_n(r) - \tilde{d}'_{n+1}(r) \right] < \epsilon. \tag{5.34}$$

The parameters for the numerical solution are: 1) N, the number of data point for the functions; 2) R, the domain of the functions dependent on space; (This also defines the domain of the Fourier transformed functions.) 3) α, the mixing parameter; 4) ϵ, the convergence parameter.

5.3   PY + OZ in Real Space

5.3.1   Percus-Yevick Equation in Bipolar Coordinates

5.3.2   The Algorithm

5.4   BGY

5.4.1   BGY in Bipolar Coordinates

5.4.2   The Algorithm

6   Perturbation Theory

6.1   General Theory and the Van Der Waals Equation

6.2   Barker-Henderson Theory

6.3   Chandler-Weeks-Anderson Theory

A   Basic Statistical Mechanics

some intro

A.1   Ensembles

A.1.1   The Microcanonical Ensemble

A.1.2   The Canonical Ensemble

A.1.3   The Grand Canonical Ensemble

A.2   Perfect Gasses

B   The Liquid-Gas Transition

C   Fourier Transformation of Spherically symmetric Functions in $\mathbb{R}^3$

The following definitions of the Fourier transformation in $\mathbb{R}^3$ are used:

$$F(\boldsymbol{k}) = \int d\boldsymbol{r} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} f(\boldsymbol{r}), \tag{C.1}$$

and

$$f(\boldsymbol{r}) = \int \frac{d\boldsymbol{k}}{(2\pi)^3} \, e^{-i\boldsymbol{r}\cdot\boldsymbol{k}} F(\boldsymbol{k}). \tag{C.2}$$

When the function $f(\boldsymbol{r})$ only depends on the absolute value of $\boldsymbol{r}$, the forward transformation becomes

$$F(\boldsymbol{k}) = \int d\boldsymbol{r} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} f(|\boldsymbol{r}|) \tag{C.3}$$

$$= \int d\boldsymbol{r} e^{ikr\cos(\theta)} f(|\boldsymbol{r}|), \tag{C.4}$$

where the real-space coordinate system is choosen such that the vector $\boldsymbol{k}$ point along the $\hat{e}_z$ axis, which is possible because of the rotational symmetry of the function $f(\boldsymbol{r})$. The angle θ is the angle with the $\hat{e}_z$ axis. This equation also makes it clear that if $f(\boldsymbol{r})$ only depends on the absolute value of $\boldsymbol{r}$, than the Fourier transformation $F(\boldsymbol{k})$ only depends on the absolute value of $\boldsymbol{k}$. Next, one can transform to a spherical coordiante system:

$$F(k) = \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^\infty dr r^2 e^{-irk\cos(\theta)} f(r) \tag{C.5}$$

$$= -2\pi \int_{\cos(0)}^{\cos(\pi)} d\left[\cos(\theta)\right] \int_0^\infty dr r^2 e^{irk\cos(\theta)} f(r) \tag{C.6}$$

$$= -2\pi \int_1^{-1} \int_0^\infty dr r^2 e^{-ikrx} f(r) \tag{C.7}$$

$$= 2\pi \int_0^\infty dr r^2 f(r) \frac{1}{-ikr} \left[e^{-ikr} - e^{ikr}\right] \tag{C.8}$$

$$= 4\pi \int_0^\infty dr r^2 f(r) \frac{\sin(kr)}{kr}. \tag{C.9}$$

In the same way the inverse transformation can be simpified:

$$f(r) = \int \frac{d\boldsymbol{k}}{(2\pi)^3} F(|\boldsymbol{k}|) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \tag{C.10}$$

$$= \frac{1}{2\pi^2} \int_0^\infty dk k^2 F(k) \frac{\sin(kr)}{kr}. \tag{C.11}$$

[2–7]

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