Fourier Space Method

The basic algorithm:

1) Guess $h_0(r)$.

2) Get $c_n(r)$ from $h_n(r)$ and the PY approximation. $\left(c(r) = f(r) e^{\beta u(r)} h(r) \right)$.

3) Fourier transform $c_n(r)$ to get $\hat{C}_n(k)$

4) Use the OZ relation in Fourier space to get $\hat{H}_{n+1}(k)$

5) Fourier transform back to get $m(r) = FT^{-1}\{\hat{H}_{n+1}\}(r)$

6) Mix Lin with $h_n(r)$

$$h_{n+1}(r) = \alpha h_n(r) + (1-\alpha) m(r) \qquad 0 \leq \alpha \leq 1$$

7) Check for convergence.
If converged: done
else: goto 2.

This algorithm will lead to multiplications and divisions by infinities. To avoid this some alterations need to be made. Before making the changes I will show you how to do the Fourier transformations and what the problem is with the PY approximation in this algorithm.

The Percus-Yevick approximation

$$c(r) = f(r)\,y(r) \qquad f(r) = e^{-\beta u(r)} - 1$$

$$y(r) = e^{\beta u(r)}\, g(r)$$

$$h(r) = g(r) - 1$$

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

$$\underbrace{c(r)}_{\text{direct correlation}} = \underbrace{h(r)}_{\text{Total correlation}} - \underbrace{\left[e^{\beta u(r)} h(r) + e^{\beta u(r)} - 1\right]}_{\text{indirect correlation.}}$$

* $c(r)$ and $h(r)$ are finite for all r so the indirect correlation is also finite, but $e^{\beta u(r)}$ goes to ∞ for Lennard-Jones or hard sphere particles. So, in the way the indirect correlations are written, there is some cancellation of infinities. This is a problem for numerical calculations, but can be avoided by using the indirect correlations instead of $h(r)$.

- Define $d(r)$ to be the indirect correlation function:

$$h(r) = c(r) + d(r)$$

- Reorder the PY approximation such that it relates $d(r)$ to $c(r)$

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

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

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

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

$f(r)$ is finite everywhere, so this eq. can be used for the numerical calculation.

The Fourier Transformation of the OZ equation

The OZ equation in real space is

$$h(|\vec{r}|) = c(|\vec{r}|) + \rho \int d^3r' \; c(|\vec{r}'|)\, h(|\vec{r}-\vec{r}'|).$$

Fourier transform both sides:

$$
\begin{aligned}
FT\left\{ \int d^3r' \, c(|\vec{r}'|)\, h(|\vec{r}-\vec{r}'|) \right\}(k)
&= \int d^3r' \, c(|\vec{r}'|) \int d^3r \; e^{-i\vec{k}\cdot\vec{r}} \, h(|\vec{r}-\vec{r}'|) \\
&= \int d^3r' \, c(|\vec{r}'|) \int d^3r \; e^{-i\vec{k}\cdot(\vec{r}+\vec{r}')} \, h(|\vec{r}|) \\
&= \int d^3r' \, e^{-i\vec{k}\cdot\vec{r}'} \, c(|\vec{r}'|) \int d^3r \; e^{-i\vec{k}\cdot\vec{r}} \, h(|\vec{r}|) \\
&= \hat{C}(k)\, \hat{h}(k)
\end{aligned}
$$

$\Rightarrow$ OZ in $\vec{k}$ space:

$$\hat{H}(k) = \hat{C}(\vec{k}) + \rho\, \hat{C}(\vec{k})\, \hat{H}(\vec{k})$$

$$\hat{H}(\vec{k}) = \frac{\hat{C}(\vec{k})}{1 - \rho\, \hat{C}(\vec{k})}$$

This equation depends on the normalization of the forward Fourier transformation

* The OZ relation gives $\hat{H}$ from $\hat{C}$, but we want to use $\hat{D}$ instead of $\hat{H}$, so we need to express $\hat{D}$ using $\hat{C}$

$$d(r) = h(r) - c(r)$$

so $\hat{D}(k) = \hat{H}(k) - \hat{C}(k)$

$$= \frac{\hat{C}(k)}{1-\rho\hat{C}(k)} - \hat{C}(k)$$

So using $d(r)$ instead of $h(r)$ solves the problem of the infinities comming from $e^{\beta h(r)}$ in the PY approximation.

$\boxed{\text{Fourier Transformation in } \mathbb{R}^3}$

One more problem:

In order to use the sine transformations you have to multiply $f(r)$ by r and divide the result by k (and similarly for the inverse transformation). It is not necessary to do this because for the inverse transformation you have to multiply by k again. To avoid all that, you can work with the functions:

$$c'(r) = r\,c(r) \qquad \hat{C}'(k) = k\,\hat{C}(k)$$
$$h'(r) = r\,h(r) \qquad \hat{H}'(k) = k\,\hat{H}(k)$$

• OZ Relation

$$\hat{D}(k) = \frac{\hat{C}(k)}{1-\rho\hat{C}(k)} - \hat{C}(k) \Rightarrow \hat{D}'(k) = \frac{\hat{C}'(k)}{1-\rho\,\hat{C}'(k)/k} - \hat{C}'(k)$$

The division $\hat{C}'(k)/k$ in the denominator need not be done because $\hat{D}'(0) = 0$, since $\hat{D}(k)$ is finite, so $k\hat{D}(k) = 0$

- The PY approximation

$$c(r) = f(r)\left[d(r)+1\right] \Rightarrow c'(r) = f(r)\left[d'(r)+r\right]$$

The final algorithm:

1) Guess $d'_0(r)$ $\quad\left[\text{eq. } d'_0(r) = \lim_{\rho\to\rho_0} d(r) = 0\right]$
2) Get $c'_n(r)$ from $d'_n(r)$ and the PY approximation.
3) Fourier transform to get $\hat{C}'_n(k)$
4) Use the OZ relation to get $\hat{D}'_{n+1}(k)$
5) Inverse Fourier transform: $m(r) = FT^{-1}\left\{\hat{D}'_{n+1}(k)\right\}(r)$
6) Mix the new solution with $d'_n(r)$:

$$d'_{n+1}(r) = \alpha\, d'_n(r) + (1-\alpha)\, m(r) \qquad 0 \le \alpha \le 1$$

7) Check for convergence.
   If converged: goto 8
   else: goto 2
8) $$h(r) = \begin{cases} -1 & r = 0 \\ c'_n(r)/r + d'_{n+1}(r)/r & r > 0 \end{cases}$$

Convergence: $\sqrt{\sum_i^N \left[d'_n(r_i) - L(r_i)\right]^2} < \epsilon$

The parameters for the numerical solution are

N, the number of data points
R, the cutoff of the r integral
α, the mixing parameter
ϵ, the convergence parameter.

Fourier Transformation of a Spherically Symmetric Real function in $\mathbb{R}^3$

* The forward transformation: $f(r) \to \hat{F}(k)$

$$\hat{F}(|\vec{k}|) = \int d^3r\, e^{-i\vec{k}\cdot\vec{r}} f(|\vec{r}|)$$

with $k = |\vec{k}|$ and $r = |\vec{r}|$

for every $\vec{k}$ you can choose the coordinate system for $\vec{r}$ such that $\vec{k}$ points along $\hat{z}$ in the $\vec{r}$ coordinates

$$\hat{F}(k) = \int d^3r\, e^{-ikr\cos\theta} f(r)$$

So if $f(\vec{r}) = f(|\vec{r}|)$ then $\hat{F}(\vec{k}) = \hat{F}(|\vec{k}|)$

$$= \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr\, r^2 e^{-ikr\cos\theta} f(r)$$

$$\int_0^{2\pi} d\varphi = 2\pi \qquad \sin\theta\, d\theta = -d[\cos\theta]$$

$$= -2\pi \int_{\theta=0}^{\theta=\pi} d[\cos\theta] \int_0^{\infty} dr\, r^2 e^{-ikr\cos\theta} f(r)$$

$$x = \cos\theta \qquad \cos(0) = 1, \quad \cos(\pi) = -1$$

$$= 2\pi \int_{-1}^{1} dx \int_0^{\infty} dr\, r^2 e^{-ikrx} f(r)$$

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

$$= 4\pi \int_0^{\infty} dr\, r^2 f(r) \frac{\sin(kr)}{kr}$$

* The inverse transformation:

$$f(r) = \int \frac{d^3k}{(2\pi)^3} \hat{F}(k) e^{i\vec{k}\cdot\vec{r}}$$

$$= \frac{1}{2\pi^2} \int_0^{\infty} dk\, k^2 \hat{F}(k) \frac{\sin(kr)}{kr}$$

If $\hat{F}(k)$ and $f(r)$ decay fast enough the integrals can be truncated at some finite value.

The discrete versions of the transformations:

$$f(r_i) = \frac{1}{2\pi^2 r_i} \sum_{i=0}^{N-1} \Delta k\, k_i \hat{F}(k_i) \sin(k_i r_i)$$

$$\hat{F}(k_i) = \frac{4\pi}{k_i} \sum_{i=0}^{N-1} \Delta r\, r_i f(r_i) \sin(k_i r_i)$$

where $r_{N-1} = R$ is the upperbound of the r integral.

N are the number of points.

$\Delta r = R/N \qquad \Delta k = \frac{K}{N} = \pi/R$

$K = \frac{N\pi}{R}$