The Percus-Yevick approximation

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This document is a review of the Percus-Yevick approximation as it is used in [2].

1 Hard spheres

For hard spheres in a particulate material without boundaries, the Percus-Yevick (P-Y) approximation [3] can be evaluated exactly. We follow [4, 5] closely, and start by defining the function

$$h(\boldsymbol{r}) = g(\boldsymbol{r}) - 1, \quad \boldsymbol{r} \in \mathbb{R}^3$$

This function satisfies the Ornstein-Zernike equation

$$h(\boldsymbol{r}) = c(\boldsymbol{r}) + n_0 \iiint_{\mathbb{R}^3} c(\boldsymbol{r}')h(\boldsymbol{r} - \boldsymbol{r}') \, \mathrm{d}v', \quad \boldsymbol{r} \in \mathbb{R}^3$$

where $c(\boldsymbol{r})$ is the direct correlation function. The integral defines the indirect correlation function $h(\boldsymbol{r})$. Ornstein-Zernike equation is of convolution type, and its Fourier transform is

$$\hat{h}(\boldsymbol{\xi}) = \hat{c}(\boldsymbol{\xi}) + n_0 \hat{c}(\boldsymbol{\xi})\hat{h}(\boldsymbol{\xi}), \quad \boldsymbol{\xi} \in \mathbb{R}^3$$

with solution

$$\hat{h}(\boldsymbol{\xi}) = \frac{\hat{c}(\boldsymbol{\xi})}{1 - n_0 \hat{c}(\boldsymbol{\xi})}, \quad \boldsymbol{\xi} \in \mathbb{R}^3$$

The structure factor $S(\boldsymbol{\xi})$ is defined as

$$S(\boldsymbol{\xi}) = 1 + n_0 \hat{h}(\boldsymbol{\xi})$$

The direct correlation function $c(\boldsymbol{r})$ is now determined. It is convenient to introduce a new function $y(\boldsymbol{r})$ as $(R = 2a)$

$$y(\boldsymbol{r}) = \begin{cases} -c(\boldsymbol{r}), & r < R \\ g(\boldsymbol{r}), & r \geq R \end{cases}$$

2 The Percus-Yevick approximation

In the P-Y approximation, we replace $h(\boldsymbol{r})-c(\boldsymbol{r})$ with $y(\boldsymbol{r})-1$ everywhere in space. We then have

$$c(\boldsymbol{r}) = \begin{cases} -y(\boldsymbol{r}), & r < R \\ h(\boldsymbol{r}) + 1 - g(\boldsymbol{r}) = 0, & r \geq R \end{cases}$$

and the Ornstein-Zernike equation becomes

$$y(\boldsymbol{r}) - 1 = -n_0 \iiint\limits_{r'<R} y(\boldsymbol{r}')(g(\boldsymbol{r}-\boldsymbol{r}') - 1)\,\mathrm{d}v', \quad \boldsymbol{r} \in \mathbb{R}^3$$

or

$$y(\boldsymbol{r}) = 1 + n_0 \iiint\limits_{\substack{r'<R \\ |\boldsymbol{r}-\boldsymbol{r}'|<R}} y(\boldsymbol{r}')\ \mathrm{d}v' - n_0 \iiint\limits_{\substack{r'<R \\ |\boldsymbol{r}-\boldsymbol{r}'|\geq R}} y(\boldsymbol{r}')(y(\boldsymbol{r}-\boldsymbol{r}') - 1)\ \mathrm{d}v'$$

This has a closed form solution for $c(\boldsymbol{r})$, $r < R$, which is [5]

$$c(\boldsymbol{r}) = c(r) = \begin{cases} \alpha + \beta(r/R) + \delta(r/R)^3, & r < R \\ 0, & r \geq R \end{cases}$$

where

$$\begin{cases} \alpha = -\dfrac{(1+2f)^2}{(1-f)^4} \\ \beta = 6f\dfrac{(1+f/2)^2}{(1-f)^4} \end{cases} \qquad \begin{cases} \delta = -f\dfrac{(1+2f)^2}{2(1-f)^4} \\ f = \dfrac{n_0 \pi R^3}{6} \end{cases}$$

with Fourier transform

$$\begin{aligned} \hat{c}(\boldsymbol{\xi}) = \hat{c}(\xi) = \iiint\limits_{\mathbb{R}^3} c(r)\mathrm{e}^{-\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{r}}\,\mathrm{d}v &= 4\pi \int_0^R \left(\alpha + \beta(r/R) + \delta(r/R)^3\right) \mathrm{j}_0(\xi r)\, r^2\,\mathrm{d}r \\ &= \frac{4\pi R^3}{\xi R} \int_0^1 \left(\alpha x + \beta x^2 + \delta x^4\right) \sin(\xi R x)\ \mathrm{d}x = 4\pi R^3 F(\xi R) \end{aligned}$$

where we introduced the function $F(x)$, defined as

$$F(x) = A(x) + B(x)\sin(x) + C(x)\cos(x) = O(1/x^2), \quad \text{as } x \to \infty \tag{2.1}$$

where

$$\begin{cases} A(x) = \dfrac{24\delta}{x^6} - \dfrac{2\beta}{x^4} \\ B(x) = \dfrac{\alpha + 2\beta + 4\delta}{x^3} - \dfrac{24\delta}{x^5} \\ C(x) = -\dfrac{\alpha + \beta + \delta}{x^2} + \dfrac{2\beta + 12\delta}{x^4} - \dfrac{24\delta}{x^6} \end{cases}$$

Finally,

$$h(\boldsymbol{r}) = h(r) = \frac{1}{8\pi^3} \iiint\limits_{\mathbb{R}^3} \frac{\hat{c}(\boldsymbol{\xi})}{1 - n_0\hat{c}(\boldsymbol{\xi})} e^{i\boldsymbol{\xi}\cdot\boldsymbol{r}} \, d\xi^3 = \frac{1}{2\pi^2 r} \int_0^\infty \frac{\hat{c}(\xi)}{1 - n_0\hat{c}(\xi)} \sin(\xi r) \, \xi \, d\xi$$

Reformulate the solution to

$$h(r) = \frac{2R}{\pi r} \int_0^\infty \frac{xF(x)}{1 - 24fF(x)} \sin(xr/R) \, dx$$

and $g(r) = h(r) + 1$.

The integral in the computation of the function $h(r)$ is poorly converging at infinity, and we need to extract the slowly converging tail. Make an asymptotic analysis of the integrand as $x \to \infty$. We get

$$\frac{xF(x)}{1 - 24fF(x)} = G(x) + O(x^{-3})$$

where

$$G(x) = (\alpha + 2\beta + 4\delta) \frac{\sin(x)}{x^2} - (\alpha + \beta + \delta) \frac{\cos(x)}{x} \tag{2.2}$$

Use the integrals [1]

$$\int_0^\infty \frac{\cos(x)\sin(\eta x)}{x} \, dx = \frac{\pi}{2}, \quad \eta > 1$$

and

$$\int_0^\infty \frac{\sin(x)\sin(\eta x)}{x^2} \, dx = \frac{\pi}{2}, \quad \eta > 1$$

to evaluate ($\eta = r/R \in [1, \infty)$)

$$h(r) = 9f \frac{1+f}{2\eta(1-f)^3} + \frac{2}{\eta\pi} \int_0^\infty \left(\frac{xF(x)}{1 - 24fF(x)} - G(x) \right) \sin(\eta x) \, dx$$

3 Examples

In Figure 1, we illustrate the calculations made in this note for different volume fractions f.

References

[1] I. S. Gradshteyn and I. M. Ryzhik. *Table of Integrals, Series, and Products.* Academic Press, San Diego, CA, seventh edition, 2007.

[2] G. Kristensson, M. Gustavsson, and N. Wellander. Multiple scattering by a collection of randomly located obstacles. Part IV: The effect of the pair correlation function. Technical Report LUTEDX/(TEAT-7272)/1–23/(2021), Department of Electrical and Information Technology, P.O. Box 118, S-221 00 Lund, Sweden, 2021.

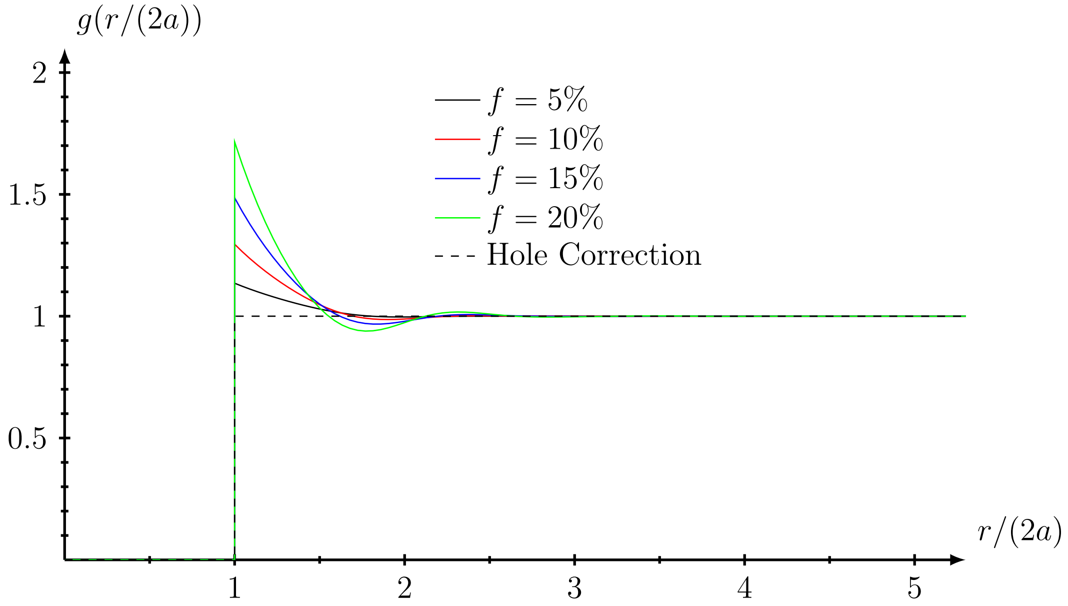

Figure 1: The hole correction (HC) and the Percus-Yevick approximation for volume fractions $f = 0.05$, $f = 0.1$, $f = 0.15$, and $f = 0.2$.

[3] J. K. Percus and G. J. Yevick. Analysis of classical statistical mechanics by means of collective coordinates. *Phys. Rev.*, **110**(1), 1, 1958.

[4] L. Tsang, J. A. Kong, K.-H. Ding, and C. O. Ao. *Scattering of Electromagnetic Waves: Numerical Simulations.* John Wiley & Sons, New York, NY, 2001.

[5] M. S. Wertheim. Exact solution of the Percus-Yevick integral equation for hard spheres. *Phys. Rev. Lett.*, **10**(8), 321–323, 1963.