Radial distribution function

Kaihang Shi

June 12, 2019

In this note, I will go over the definition of the radial distribution function and derive the expression that can be used in the computer simulation.

The radial distribution function arises from the 2-body density distribution function. For a homogeneous system, the radial distribution function is given by [1]

$$g(\mathbf{r}_1,\mathbf{r}_2)=\frac{\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)}{\rho^2} \tag{1}$$

Where the bulk density of the system is ρ and the 2-body distribution function is

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=\frac{N(N-1)}{Z}\int \exp(-\beta U)\,d\mathbf{r}_3 d\mathbf{r}_4 ... d\mathbf{r}_N \tag{2}$$

Where Z is the configurational partition function and N is the total number of particles. Now we integrate Eq. (1) over the position of particle 1 and particle 2,

$$\int\int g(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2=\frac{\int\int \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2}{\rho^2} \tag{3}$$

Due to the translational invariance in the homogeneous system, we can set position of particle 1 as the origin, and Eq. (3) becomes,

$$\int\int g(r)\,d\mathbf{r}_1 4\pi r^2 dr=\frac{N(N-1)}{\rho^2} \tag{4}$$

Remembering

$$\int\int \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2=N(N-1) \tag{5}$$

Carrying out the integral with respect to the vector $\mathbf{r}_1$ in Eq. (4), we have for a large N,

$$\rho\int g(r)4\pi r^2 dr=N-1\approx N \tag{6}$$

Equivalently,

$$g(r) = \frac{dN}{\rho 4\pi r^2 dr} \quad (7)$$

Where dN is the number of particles found in an infinitesimal spherical shell in volume of $4\pi r^2 dr$. The radial distribution function is an "average" measure of deviation from the complete randomness of the homogeneous system. In practice, we will compute g(r) by averaging it over the reference particles (i.e., by setting each reference particle as the origin when measuring g(r)). Thus, in computer simulation, we have to divide the Eq. (7) by the total number of reference particle N_{ref} in the system (usually $N = N_{ref}$),

$$\overline{g}(r) = \frac{dN}{N_{ref}\rho 4\pi r^2 dr} \quad (8)$$

Reference

[1] J.-P. Hansen, I.R. McDonald, J.-P. Hansen, I.R. McDonald, Chapter 2 – Statistical Mechanics, in: Theory Simple Liq., 2013: pp. 13–59. doi:10.1016/B978-0-12-387032-2.00002-7.