$g(r)$

DF

1. Correction to text about Eqn.5.1.48 (radial distribution function)

1.1. What is the issue ? Fengyu Xi brought it to my attention that there is a sign problem in some steps in Equation 5.1.48. Below, I correct and expand the derivation of 5.1.48.

1.2. Resolution. The value of the radial distribution function at a distance r from a reference particle is equal to the angular average of $\rho(\mathbf{r})/\rho$:

$$g(r) = \frac{1}{\rho}\int d\hat{\mathbf{r}}\ \langle \rho(\mathbf{r})\rangle_{N-1} = \frac{1}{\rho}\int d\hat{\mathbf{r}}\ \left\langle \sum_{j\neq i} \delta(\mathbf{r}-\mathbf{r}_j)\right\rangle_{N-1}, \tag{5.1.44}$$

where N is the total number of particles in the system, ρ denotes the average number density ($\rho \equiv (N/V)$) and $\mathbf{r}_j$ is the distance of particle j from the origin, where particle i is located (Note: this means that $\mathbf{r}_j$ is actually $\mathbf{r}_{ij}$). $\hat{\mathbf{r}}$ is the unit vector in the direction of $\mathbf{r}$. For simplicity we have written down the expression for $g(r)$ for a given particle i, and hence the sum of $j \neq i$ is keeping i fixed, but in practice the expression is averaged over all equivalent particles i. The angular brackets denote the thermal average

$$\langle \cdots \rangle_{N-1} \equiv \frac{\int d\mathbf{r}^{N-1}\ e^{-\beta U(\mathbf{r}^N)}(\cdots)}{\int d\mathbf{r}^{N-1}\ e^{-\beta U(\mathbf{r}^N)}}, \tag{5.1.45}$$

where we integrate over $N-1$ coordinates, because particle i is held fixed.

We can now write

$$\left(\frac{\partial g(r)}{\partial r}\right) = \frac{1}{\rho}\frac{\partial}{\partial r}\int d\hat{\mathbf{r}}\ \left\langle \sum_{j\neq i} \delta(\mathbf{r}-\mathbf{r}_j)\right\rangle \tag{5.1.46}$$

The only term that depends on r (the length of $\mathbf{r}$) is the δ-function. We can therefore write

$$\left(\frac{\partial g(r)}{\partial r}\right) = \frac{1}{\rho}\int d\hat{\mathbf{r}}\ \left\langle \sum_{j\neq i} \hat{\mathbf{r}}\cdot\nabla_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}_j)\right\rangle \tag{5.1.47}$$

The following sentence was incorrect: *As the argument of the δ-function is $\mathbf{r}-\mathbf{r}_j$, we can replace $\hat{\mathbf{r}}\cdot\nabla_{\mathbf{r}}$ by $-\hat{\mathbf{r}}_j\cdot\nabla_{\mathbf{r}_j}$ and perform a partial integration.* This sentence is wrong, because $\hat{\mathbf{r}}$

is only replaced by $\hat{\mathbf{r}}_j$ after the partial integration:

$$\begin{aligned}
\left(\frac{\partial g(r)}{\partial r}\right) &= \frac{1}{\rho}\frac{\int d\hat{\mathbf{r}} \int d\mathbf{r}^{N-1}\, e^{-\beta U(\mathbf{r}^N)} \sum_{j\neq i} \hat{\mathbf{r}}\cdot\nabla_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}_j)}{\int d\mathbf{r}^{N-1}\, e^{-\beta U(\mathbf{r}^N)}} \\
&= \frac{-1}{\rho}\frac{\int d\hat{\mathbf{r}} \int d\mathbf{r}^{N-1}\, e^{-\beta U(\mathbf{r}^N)} \sum_{j\neq i} \hat{\mathbf{r}}\cdot\nabla_{\mathbf{r}_j}\delta(\mathbf{r}-\mathbf{r}_j)}{\int d\mathbf{r}^{N-1}\, e^{-\beta U(\mathbf{r}^N)}} \\
&= \frac{-\beta}{\rho}\frac{\int d\hat{\mathbf{r}} \int d\mathbf{r}^{N-1}\, e^{-\beta U(\mathbf{r}^N)} \sum_{j\neq i} \delta(\mathbf{r}-\mathbf{r}_j)\hat{\mathbf{r}}\cdot\nabla_{\mathbf{r}_j}U(\mathbf{r}^N)}{\int d\mathbf{r}^{N-1}\, e^{-\beta U(\mathbf{r}^N)}} \\
&= \frac{\beta}{\rho}\int d\hat{\mathbf{r}} \left\langle \sum_{j\neq i} \delta(\mathbf{r}-\mathbf{r}_j)\hat{\mathbf{r}}_j\cdot\mathbf{F}_j(\mathbf{r}^N)\right\rangle_{N-1} \qquad (5.1.48)
\end{aligned}$$

where $\hat{\mathbf{r}}_j\cdot\mathbf{F}_j \equiv F_j^{(r)}$ denotes the force on particle j in the radial direction. NOTE: In step 2, I replace differentiation of the delta function with respect to $\mathbf{r}$ by differentiation with respect to $-\mathbf{r}_j$. Step 3: partial integration. Here it is important to note that $\mathbf{r}$ does not depend in $\mathbf{r}_j$. However, in step 3, we then use the fact that the delta function imposes $\mathbf{r}=\mathbf{r}_j$.

We can now integrate with respect to r

$$\begin{aligned}
g(r) &= g(r=0) + \frac{\beta}{\rho}\int_0^r dr' \int d\hat{\mathbf{r}}' \left\langle \sum_{j\neq i} \delta(\mathbf{r}'-\mathbf{r}_j)F_j^{(r)}(\mathbf{r}^N)\right\rangle_{N-1} \\
&= g(r=0) + \frac{\beta}{\rho}\int_{r'<r} d\mathbf{r}' \left\langle \frac{\sum_{j\neq i} \delta(\mathbf{r}'-\mathbf{r}_j)F_j^{(r)}(\mathbf{r}^N)}{4\pi r'^2}\right\rangle_{N-1} \\
&= g(r=0) + \frac{\beta}{\rho}\sum_j \left\langle \theta(r-r_j)\frac{F_j^{(r)}(\mathbf{r}^N)}{4\pi r_j{}^2}\right\rangle_{N-1} \qquad (5.1.49)
\end{aligned}$$

where θ denotes the Heaviside step function. To make a connection to the results of Borgis *et al.*, we note that in a homogeneous system, all particles i of the same species are equivalent. We can therefore write

$$g(r) = g(r=0) + \frac{\beta}{N\rho}\sum_{i=1}^N \sum_{j\neq i} \left\langle \theta(r-r_{ij})\frac{F_j^{(r)}(\mathbf{r}^N)}{4\pi r_{ij}^2}\right\rangle_{N-1} .$$

But i and j are just dummy indices. So we obtain the same expression for $g(r)$ by permuting i and j, except that if $\hat{\mathbf{r}} = \hat{\mathbf{r}}_{ij}$, then $\hat{\mathbf{r}} = -\hat{\mathbf{r}}_{ji}$. Adding the two equivalent expressions for $g(r)$ and dividing by two, we get

$$g(r) = g(r=0) + \frac{\beta}{2N\rho}\sum_{i=1}^N \sum_{j\neq i} \left\langle \theta(r-r_{ij})\frac{F_j^{(r)}(\mathbf{r}^N) - F_i^{(r)}(\mathbf{r}^N)}{4\pi r_{ij}{}^2}\right\rangle_{N-1} \qquad (5.1.50)$$

equation (5.1.50) is equivalent to the result of Borgis *et al.*.

The remarkable feature of equation (5.1.50) is that $g(r)$ depends not just on the number of pairs *at* distance r, but on *all* pair distances less than r. We stress that we have not assumed that the interactions in the system are pairwise additive: $F_i - F_j$ is *not* a pair force.