Errata

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.

2. THE WIDTH OF A GAUSSIAN CHARGE CLOUD

Benjamin Rotenberg pointed out that Section 11.2 contains a typo:
The width of the Gaussian distribution (middle of page 376) is of course not $\sqrt{2/\alpha}$ as written, but $\sqrt{1/(2\alpha)}$

3. Maxwell-Stefan expression for diffusion coefficient

Thejas Hulikal Chakrapani pointed out there is a typographical error in Chapter 5, Illustration 3 (Diffusion coefficients), which is repeated twice.

First of all, Eqn. 5.2.18 should read

$$J(c) \equiv -\frac{L(c)}{k_B T}\nabla\mu = -\frac{cD^c(c)}{k_B T}\nabla\mu.$$

rather than

$$J(c) \equiv -\frac{L(c)}{k_B T}\nabla\mu = -\frac{D^c(c)}{k_B T c}\nabla\mu.$$

The error also affects the next equation, which should read:

$$D^t = D^c \frac{c}{k_B T}\frac{\partial\mu}{\partial \ln c}\frac{\partial \ln c}{\partial c} = \Gamma D^c,$$

But the following equation for Γ, the thermodynamic coefficient, is correct

$$\Gamma = \frac{1}{k_B T}\frac{\partial\mu}{\partial \ln c} = \frac{\partial \ln f}{\partial \ln c},$$

where we have replaced the chemical potential by the logarithm of the fugacity

Additions

1. Statistical errors in numerical quadrature

1.1. **What is the issue ?** In Chapters 8 and 9, and in Appendix N, we refer to the use of Gauss-Legendre quadrature to approximate the definite integrals that are used in thermodynamic integration.

The quadrature results in possible systematic errors, which tend to be quite small if enough quadrature points are used and if the integration variables are chosen judiciously, and statistical errors due to the fact that the quantity that we integrate is obtained by sampling and is, therefore, subject to fluctuations.

Knowing the variance in the sampled integrands allows us to estimate the statistical error in the estimate of the integral. The quadrature used need not be Gauss-Legendre.

1.2. **Error estimates.** Consider an integral

$$I = \int_a^b dx\ f(x) \tag{1}$$

We represent the integral by a Gauss-Legendre (GL) quadrature I' [1]

$$I' = (b-a)\sum_i w_i f(x_i) \tag{2}$$

where $x_i \equiv a + \lambda_i(b-a)$ and $0 < \lambda_i < 1$ is the scaled coordinate of the i-th GL point. w_i is the weight of the i-th point in the GL quadrature. We assume that the w_i are normalized, such that $\sum_{i=1}^n w_i = 1$, where n is the number of GL points.

If we obtain $f(x_i)$ by sampling, it will be subject to statistical error:

$$\sigma_i^2 =< f_i^2 > - < f_i >^2 \tag{3}$$

The error in I', $\sigma^2(I')$ depends on the variance of the individual i data points Then

$$\sigma_i^2(I') = (b-a)^2 \left[< (\sum_i w_i f(x_i))^2 > - < \sum_i w_i f(x_i) >^2 \right] \tag{4}$$

as the fluctuations in the estimates of different data points are uncorrelated and as the average fluctuation in any data point vanishes, we can write:

$$\sigma_i^2(I') = (b-a)^2 \sum_i w_i^2 < \sigma_i^2 > \tag{5}$$

Hence, you just do one simulation to compute $< f(x_i) >$ and $< f^2(x_i) >$. We then get $\sigma_i^2 =< f_i^2 > - < f_i >^2$, and this immediately yields the estimated error in the GL quadrature...

[1] We mention Gauss-Legendre here, but the arguments below apply just as well to other quadratures