Contents

Chapter 1

Errata

5.1 Correction to text before Eqn.5.1.48 (radial distribution function)

Fengyu Xi brought it to our attention that there is a sign problem in some steps in Equation (5.1.48). However, the resulting equation itself was correct. Below, we correct and expand the derivation of (5.1.48).

The incorrect sentence was the following: "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 was wrong because, in Equation (5.1.49), $\hat{\mathbf{r}}$ is only replaced by $\hat{\mathbf{r}}_j$ *after* the partial integration:

$$
\begin{aligned}
\left(\frac{\partial g(r)}{\partial r} \right) &= \frac{1}{\rho} \frac{\int d\hat{\mathbf{r}} \int d\mathbf{r}^{N-1} \, e^{-\beta U(\mathbf{r}^N)} \sum_{j \neq i} \hat{\mathbf{r}} \cdot \nabla_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_j)}{\int d\mathbf{r}^{N-1} \, e^{-\beta U(\mathbf{r}^N)}} \\[2mm]
&= \frac{-1}{\rho} \frac{\int d\hat{\mathbf{r}} \int d\mathbf{r}^{N-1} \, e^{-\beta U(\mathbf{r}^N)} \sum_{j \neq i} \hat{\mathbf{r}} \cdot \nabla_{\mathbf{r}_j} \delta(\mathbf{r} - \mathbf{r}_j)}{\int d\mathbf{r}^{N-1} \, e^{-\beta U(\mathbf{r}^N)}} \\[2mm]
&= \frac{-\beta}{\rho} \frac{\int d\hat{\mathbf{r}} \int d\mathbf{r}^{N-1} \, e^{-\beta U(\mathbf{r}^N)} \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_j) \hat{\mathbf{r}} \cdot \nabla_{\mathbf{r}_j} U(\mathbf{r}^N)}{\int d\mathbf{r}^{N-1} \, e^{-\beta U(\mathbf{r}^N)}} \\[2mm]
&= \frac{\beta}{\rho} \int d\hat{\mathbf{r}} \left\langle \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_j) \hat{\mathbf{r}}_j \cdot \mathbf{F}_j(\mathbf{r}^N) \right\rangle_{N-1}
\end{aligned}
$$

$$(5.1.49)$$

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, we replaced 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 on $\mathbf{r}_j$. Only in step 3 we then use the fact that the delta function imposes $\mathbf{r} = \mathbf{r}_j$.

5.2 Maxwell-Stefan diffusion (Illustration 3)

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.

5.2   Dynamical Properties (5.2.2: O(n) algorithm)

Order-n algorithm for computing correlation functions

Amin Bakhshandeh pointed out an error in Figure 5.8, section 5.2.2, which is meant to illustrate the coarse-graining procedure to measure time-correlation functions in order-n time. In the top line of the figure, the symbols n and j had been permuted. The corrected Figure 5.8 is shown below.
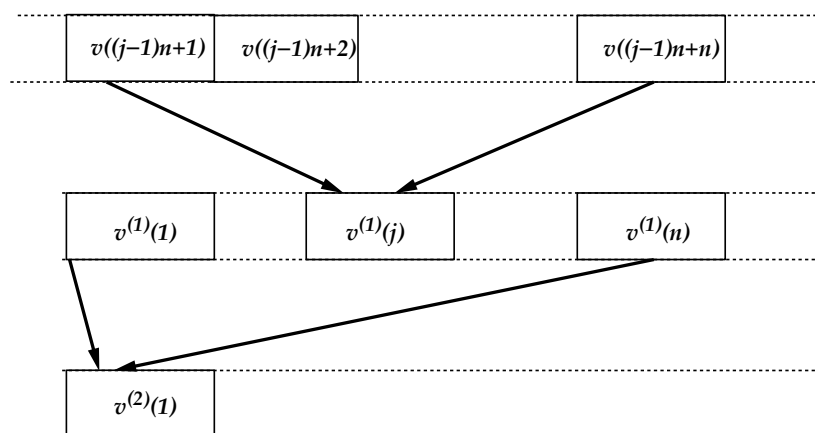
Figure 5.8: Coarse graining the velocities.

8.6 Piecing free-energy profiles together: MBAR

Michael Allen pointed out that there was a serious mix-up of indices in the original text of section 8.6.11. Below, the corrected expressions are given. The corrections are highlighted in red.

The key idea underlying MBAR is that we have information only for those points that have been sampled. Imagine that we had sampled only one point, at coordinate $\mathcal{X}_i$, then our best estimate for $P(\mathcal{X})$ would be $P(\mathcal{X})=\delta(\mathcal{X}-\mathcal{X}_i)$. If, instead, we have performed K simulations at different bias potentials V_k ($k=\{1, 2, \cdots, K\}$), with N_k points for bias V_k, then MBAR assumes that $P(\mathcal{X})$ must be of the form

$$P(\mathcal{X}) = \mathcal{Z}^{-1} \sum_{k=1}^{K} \sum_{n=1}^{N_k} p_{k,n} \delta(\mathcal{X} - \mathcal{X}_{k,n}) \ , \tag{8.6.49}$$

where

$$\mathcal{Z} \equiv \sum_{k=1}^{K} \sum_{n=1}^{N_k} p_{k,n} \ . \tag{8.6.50}$$

At this stage, the weights $p_{k,n}$ are unknown. However, once we have determined the $p_{k,n}$, we can use equation (8.6.28) to write the biased distributions:

$$P_j(\mathcal{X}) = \mathcal{Z}_j^{-1} \sum_{k=1}^{K} \sum_{n=1}^{N_k} p_{k,n} \exp\left[-\beta V_j(\mathcal{X})\right] \delta(\mathcal{X} - \mathcal{X}_{k,n}) \ , \tag{8.6.51}$$

with

$$\mathcal{Z}_j \equiv \sum_{k=1}^{K} \sum_{n=1}^{N_k} p_{k,n} \exp\left[-\beta V_j(\mathcal{X}_{k,n})\right] \ . \tag{8.6.52}$$

We determine $p_{k,n}$ by considering the likelihood of the observed sample. The likelihood L is the probability that the observed set of points would be generated for a given set $p_{k,n}$:

$$L \equiv \prod_{k=1}^{K} \left[\prod_{n=1}^{N_k} P_k(\mathcal{X}_{k,n}) \right] \ . \tag{8.6.53}$$

Clearly, L depends on all $p_{k,n}$. We can make this explicit by inserting the expression for P_k in the above equation or, what is more convenient, in the expression for $\ln L$:

$$\ln L \equiv \sum_{k=1}^{K} \sum_{n=1}^{N_k} \ln \frac{p_{k,n}}{\mathcal{Z}_k} \exp\left[-\beta V_k(\mathcal{X}_{k,n})\right] \ . \tag{8.6.54}$$

To maximize the likelihood, we must differentiate with respect to all $p_{k,n}$ to find the condition for $\partial \ln L / \partial p_{k,n} = 0$: Note that only $\ln p_{k,n}$ and the $\mathcal{Z}_j$ depend on $p_{k,n}$. In particular, $V_k(\mathcal{X}_{k,n})$ does not depend on $p_{k,n}$. Hence, we must differentiate:

$$
\begin{aligned}
\ln L &= \text{constant} + \sum_{k=1}^{K} \sum_{n=1}^{N_k} [\ln p_{k,n} - \ln \mathcal{Z}_k] \\
&= \text{constant} + \sum_{k=1}^{K} \sum_{n=1}^{N_k} \ln p_{k,n} - \sum_{k=1}^{K} N_k \ln \mathcal{Z}_k \ .
\end{aligned}
\tag{8.6.55}
$$

In the second line of equation (8.6.55) we have used the fact that the second sum over n yields simply N_k times the same term. The condition for maximum likelihood is then:

$$
0 = \frac{1}{p_{k,n}} - \sum_{j=1}^{K} N_j \frac{\exp[-\beta V_j(\mathcal{X}_{k,n})]}{\mathcal{Z}_j} \ .
\tag{8.6.56}
$$

We can now write an expression for $p_{k,n}/\mathcal{Z}$:

$$
p_{k,n}/\mathcal{Z} = \frac{1}{\sum_{j=1}^{K} N_j \frac{\exp[-\beta V_j(\mathcal{X}_{k,n})]}{(\mathcal{Z}_j/\mathcal{Z})}} \ .
\tag{8.6.57}
$$

Having determined the weights $p_{k,n}$, the ratio $\mathcal{Z}/\mathcal{Z}_j$ is our best estimate for Z/Z_j, and hence $\mathcal{Z}_j/\mathcal{Z} = \exp(-\beta \Delta F_j)$. It then follows that

$$
p_{k,n}/\mathcal{Z} = \frac{1}{\sum_{j=1}^{K} N_j \exp\left[-\beta(V_j(\mathcal{X}_{k,n}) - \Delta F_j)\right]} \ .
\tag{8.6.58}
$$

Finally, we can insert this expression for $p_{k,n}$ in equation (8.6.52) to obtain an expression for $\mathcal{Z}_i/\mathcal{Z}$ and thereby for ΔF_i:

$$
\Delta F_i = -k_B T \ln \sum_{k=1}^{K} \sum_{n=1}^{N_k} \frac{\exp[-\beta V_i(\mathcal{X}_{k,n})]}{\sum_{j=1}^{K} N_j \exp\left[-\beta(V_j(\mathcal{X}_{k,n}) - \Delta F_j)\right]} \ .
\tag{8.6.59}
$$

Note that this is an implicit equation that has to be solved self-consistently for all ΔF_i.

7.1 Stochastic global energy rescaling

Michael Allen pointed out that there are errors in the equations describing the corrected "Heyes" thermostat on page 257. Below, we highlight the corrections in red:

... the equilibrium distribution of the total kinetic energy E_k at inverse temperature β is:

$$P(E_k) = \mathcal{C} E_k^{d(N-1)/2-1} \exp(-\beta E_k) \,,$$

where $\mathcal{C}$ is an (unimportant) normalization constant.

In the original text, we wrote $d(N-1)$ instead of $d(N-1)/2-1$ in the exponent of the kinetic energy. The correct results can be derived as follows: first, because momentum-scaling thermostats only work correctly if the total momentum is zero (and therefore remains zero upon rescaling), the number of independent momenta is equal to $d(N-1) \equiv f$, where f denotes the number of independent degrees of freedom.

Now consider the Boltzmann distribution of these momenta. We write the kinetic energy E_k as $E_k = \sum_{i=1}^{N} p_i^2/(2m_i)$. For the sake of convenience, we assume that all masses are the same. However, if this is not the case, it is important to remember that, if the masses of the particles are different, conserving (zero) momentum is not equivalent to conserving zero *average* particle velocity (as opposed to zero center-of-mass velocity), and conversely. With equal masses, the hyper-surface of constant kinetic energy is a (hyper)sphere in momentum-space with radius $p_t \equiv \sqrt{\sum p_i^2}$, such that $E_k \sim p_t^2/2m$ Then

$$P_B(\mathbf{p}^f)d\mathbf{p}^f \sim P_B(\mathbf{p}^f)p_t^{f-1}dp_t \sim P_B(E_k)E_k^{(f-1)/2-1/2}dE_k$$

Therefore, $P(E_k)$, the kinetic energy distribution (again, ignoring the constant normalization factor) is

$$P(E_k) = P_B(E_k)E_k^{f/2-1}$$

Inserting $f = d(N-1)$, we arrive at the desired result.

The missing factor $1/2$ in the uncorrected expression comes back in the acceptance rule, which should be corrected to:

$$\text{acc}(E_k \to E'_k) = \min\left(1, z^{d(N-1)} e^{-\beta E_k(z^2-1)}\right) \,.$$

11.3   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 $\sqrt{1/(2\alpha)}$

Chapter 2

Additions

2.1 Statistical errors in numerical quadrature

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.

Error estimates

Consider an integral

$$I = \int_a^b dx\ f(x) \tag{2.1.1}$$

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

$$I' = (b-a) \sum_i w_i f(x_i) \tag{2.1.2}$$

---

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

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:

$$\sigma_i^2 = < f_i^2 > - < f_i >^2 \tag{2.1.3}$$

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

$$\sigma_i^2(I') = (b - a)^2 \left[< (\sum_i w_i f(x_i))^2 > - < \sum_i w_i f(x_i) >^2 \right] \tag{2.1.4}$$

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:

$$\sigma_i^2(I') = (b - a)^2 \sum_i w_i^2 < \sigma_i^2 > \tag{2.1.5}$$

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...