The 'constant salt ensemble'

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Abstract

Rough investigation of the ensemble and acceptance test used for constant counterion Monte Carlo simulations as initiated by John Chodera.

1 The model

The aim is to simulate a region that exchanges molecules with a bath of bulk water with a fixed concentration of NaCl. The simulated region and bath are labeled a and b, with volumes V_a and V_b respectively. Like in the Gibbs ensemble, the interaction energy between the two compartments is zero. Both compartments will have a neutral charge. The total volume, $V_a + V_b$, is constant, and we shall initially assume that subvolumes are also constant, although this can be relaxed later. The total number of molecules, N, is constant, and is decomposed

$$N = n_w^a + n_w^b + n_{Na}^a + n_{Na}^b + n_{Cl}^a + n_{Cl}^b, \tag{1}$$

where n_w^a denotes the number of water molecules in compartment a, n_w^b the number of water molecules in compartment b, and similarly for sodium and chlorine. The probability density for observing compartment a and b with a configuration $(\mathbf{x}_a, \mathbf{x}_b)$ and set of compartment species numbers $\mathbf{n} = (n_w^a, n_w^b, n_{Na}^a, n_{Na}^b, n_{Cl}^a, n_{Cl}^b)$ is given by

$$\pi(\mathbf{x}_a, \mathbf{x}_b, \mathbf{n} | \beta, V_a, V_b) \propto \prod_{i,j} \frac{V_i^{n_j^i}}{n_j^i! \, \Lambda^{3n_j^i}} \, e^{-u(\mathbf{x}_a, \mathbf{x}_b)} \tag{2}$$

where $i \in \{a, b\}$, $j \in \{w, Na, Cl\}$, and $u(\mathbf{x}_a, \mathbf{x}_b)$ is the dimentionless interaction energy.

2 Acceptance test derivation

To avoid the creation and annihaltion of particles and to keep the simulated region (compartment a) neutral, exchange moves involve simultaneously swapping two water molecules for Na and Cl. The acceptance probability will be derived by evaluating the acceptance probability for each stage of the swap individually, then amalgamating them all in a single move and acceptance probability.

For sampling exchanges with the Metropolis-Hastings algorithm with symmetric transition probabilities, the acceptance probability for removing one particle labeled i (i.e. Na or Cl) from compartment b and adding it to a, but maintaining a fixed configuration (i.e. an identity exchange) is given by

$$A(n_i^a, n_i^b \to n_i^a + 1, n_i^b - 1 | \mathbf{x}_a, \mathbf{x}_b) = \frac{\pi(n_i^a + 1, n_i^b - 1)}{\pi(n_i^a, n_i^b)}$$

$$= \frac{V_a}{V_b} \frac{n_i^b}{n_i^a + 1} e^{-\Delta u_i(\mathbf{x}_a) - \Delta u_i(\mathbf{x}_b)}. \tag{3}$$

The acceptance probability to exchange two water molecules from a to b is composed of two annhilations from a and two creations in b. Because the interaction energy between compartments a and b is zero, $A(n_w^a, n_w^b \to n_w^a - 2, n_w^b + 2) = A(n_w^a \to n_w^a - 2)A(n_w^b \to n_w^b + 2)$. For the first term on the LHS, we have

$$A(n_w^a \to n_w^a - 2 | \mathbf{x}_a, \mathbf{x}_b) = \frac{\pi(n_w^a - 2)}{\pi(n_w^a)}$$

$$= \frac{n_w^a(n_w^a - 1)(\Lambda_w)^6}{(V_a)^2} e^{-\Delta u_w(\mathbf{x}_a)}, \tag{4}$$

and for the second term of the LHS we have

$$A(n_w^b \to n_w^b + 2 | \mathbf{x}_a, \mathbf{x}_b) = \frac{\pi(n_w^b + 2)}{\pi(n_w^b)}$$

$$= \frac{(V_b)^2}{(n_w^b + 1)(n_w^b + 2)(\Lambda_w)^6} e^{-\Delta u_w(\mathbf{x}_b)}, \tag{5}$$

so that

$$A(n_w^a, n_w^b \to n_w^a - 2, n_w^b + 2 | \mathbf{x}_a, \mathbf{x}_b) = \left(\frac{V_b}{V_a}\right)^2 \frac{n_w^a(n_w^a - 1)}{(n_w^b + 1)(n_w^b + 2)} e^{-\Delta u_w(\mathbf{x}_a) - \Delta u_w(\mathbf{x}_b)}. \tag{6}$$

Therefore, the total acceptance probability for removing one atom of Na and one atom of Cl from compartment b, and adding them to compartment a, whilst simulaneously removing two water molecules from a and adding them to b is given by

$$A(\mathbf{n}_{initial} \to \mathbf{n}_{final} | \mathbf{x}_a, \mathbf{x}_b) = \frac{n_w^a(n_w^a - 1)}{(n_w^b + 1)(n_w^b + 2)} \frac{n_{Na}^b n_{Cl}^b}{(n_{Na}^a + 1)(n_{Cl}^a + 1)} e^{-\Delta u(\mathbf{x}_a) - \Delta u(\mathbf{x}_b)}, \tag{7}$$

where $U(\mathbf{x}_a)$ and $\Delta U(\mathbf{x}_b)$ are the total changes in potential energy between compartments a and b.

We consider the case when compartment b (the bulk water and salt bath) becomes macroscopic in size. Collecting all the terms that correspond to b and taking the thermodynamic limits $V_b \to \infty$, $n_i^b \to \infty$, and $n_i^b / V_b \to \rho_i \; \forall \, i$, we find that

$$A(\mathbf{n}_{initial} \to \mathbf{n}_{final} | \mathbf{x}_a, \mathbf{x}_b) \to \frac{\rho_{Na}^b \rho_{Cl}^b}{(\rho_w^b)^2} \frac{n_w^a(n_w^a - 1)}{(n_{Na}^a + 1)(n_{Cl}^a + 1)} e^{\Delta u(\mathbf{x}_a) - \Delta u(\mathbf{x}_b)}$$

$$= \left(\frac{\rho_{NaCl}^b}{\rho_w^b}\right)^2 \frac{n_w^a(n_w^a - 1)}{(n_{Na}^a + 1)(n_{Cl}^a + 1)} e^{\Delta u(\mathbf{x}_a) - \Delta u(\mathbf{x}_b)}, \tag{8}$$

where the second line follows from the stoichiometry of neutral salt. Finally, we require that the macroscobic bath is unobserved, so will use the acceptance probability averaged over all configurations of x_b

$$A(\mathbf{n}_{initial} \rightarrow \mathbf{n}_{final}|\mathbf{x}_a) = \int_{V_b} \pi(\mathbf{x}_b)\, A(\mathbf{n}_{initial} \rightarrow \mathbf{n}_{final}|\mathbf{x}_a, \mathbf{x}_b)\, d\mathbf{x}_b$$

$$= \left(\frac{\rho^b_{NaCl}}{\rho^b_w}\right)^2 \frac{n^a_w(n^a_w - 1)}{(n^a_{Na} + 1)(n^a_{Cl} + 1)} \exp(-\Delta u(\mathbf{x}_a))\langle \exp - \Delta u(\mathbf{x}_b))\rangle_b$$

$$= \left(\frac{\rho^b_{NaCl}}{\rho^b_w}\right)^2 \frac{n^a_w(n^a_w - 1)}{(n^a_{Na} + 1)(n^a_{Cl} + 1)} e^{-\Delta u(\mathbf{x}_a)} \left\langle e^{-\Delta u(\mathbf{x}_b)} \right\rangle_b$$

$$= \frac{n^a_w(n^a_w - 1)}{(n^a_{Na} + 1)(n^a_{Cl} + 1)} e^{-\Delta u(\mathbf{x}_a)} \left[\left(\frac{\rho^b_{NaCl}}{\rho^b_w}\right)^2 e^{-\Delta f}\right], \tag{9}$$

where Δf is the dimentionless free energy to decouple NaCl from bulk water at a given concentration minus the free energy to couple two water molecules from bulk water. Note that the terms within the square bracket are completely determined by the thermodynamic bath. At low $NaCl$ concentrations, Δf can be evaluated via alchemical free energy calculations although in general, it is a free parameter that requires calibration. In contrast, ρ_{NaCl} and ρ_w are set by the user. Note that at low salt concentrations, it should be agree with debouble decoupling free energy calculations.

The acceptance test above is corresponds to the semi grand canonical ensemble. The identity exchange has no dependance on V_a, so volume can fluctuate during the simulation.