The Wang-Landau Reaction Ensemble Method: Simulation of Weak Polyelectrolytes and General Acid-Base Reactions

SUPPLEMENTARY MATERIAL

Jonas Landsgesell, Christian Holm, and Jens Smiatek[*]

Institute for Computational Physics, University of Stuttgart, D-70569 Stuttgart, Germany

E-mail: smiatek@icp.uni-stuttgart.de

1 Calculation of the kinetic partition sum

Via asymptotic analysis in the thermodynamic limit $N_{i\to\infty}$ and $V \to \infty$ with constant concentrations, one can derive an alternative formulation of the original reaction ensemble acceptance transition probability as described in the main article which reads

$$p_{k\to l}^{\mathrm{RE},\xi} = \min\left(1, \left(\frac{K_{\mathrm{a,input}}}{K_{\mathrm{a,\ new\ state}}}\right)^{\xi} \exp(-\beta\Delta E_{\mathrm{pot,\ k\to l}})\right), \tag{1}$$

with $K_{\mathrm{a,\ new\ state}}$ representing the value of the equilibrium constant by the law of mass action if the system is in the proposed reaction state. For numbers of titrable groups $N_0 \approx 50$, the above shown expression is already in good agreement with the expression in the main article. Thus, for an ideal gas without potential energy, the transition probability for a protonation

reaction $H^+ + A^- \rightarrow HA$ with $\xi = -1$ in the Wang-Landau reaction ensemble reads

$$p_{\bar{n}\rightarrow\bar{n}+\Delta\bar{n}} = \min\left(1, \left(\frac{K_{a,\text{input}}}{K_a(\bar{n} + \Delta\bar{n})}\right)^{-1} \frac{Z_{\text{kin}}(\bar{n})}{Z_{\text{kin}}(\bar{n} + \Delta\bar{n})}\right), \tag{2}$$

with the values for the discrete degree of association $\Delta\bar{n}$. The apparent reaction constant is known from the law of mass action and can be expressed by

$$K_a(\bar{n}) = \frac{1}{V}\frac{N_{\text{H}^+}(\bar{n})N_{\text{A}^-}(\bar{n})}{N_{\text{HA}}(\bar{n})} = c_0\frac{(1-\bar{n})^2}{\bar{n}} \tag{3}$$

as a function of the degree of association $\bar{n}$ and the number of titrable groups N_0 resulting in the concentration c_0. In a simulation with a finite number of titrable units, the smallest allowed change in the degree of association for a single reaction is given by $\Delta\bar{n} = 1/N_0$. We assume that for a fully converged density of states calculation a random walk is performed where every proposed reaction is accepted with probability $p_{\bar{n}\rightarrow\bar{n}+\Delta\bar{n}} = 1$. The resulting expression

$$\left(\frac{K_{a,\text{input}}}{K_a(\bar{n} + \Delta\bar{n})}\right)^{-1} \frac{Z_{\text{kin}}(\bar{n})}{Z_{\text{kin}}(\bar{n} + \Delta\bar{n})} = 1 \tag{4}$$

can be interpreted as a recursion formula for $Z_{\text{kin}}(\bar{n})$. Without loss of generality, we start with the value $Z_{\text{kin}}(\bar{n} = 0) = 1$ for the evaluation of Eqn. 4 and the next incremented value gives

$$Z_{\text{kin}}(\Delta\bar{n}) = \left(\frac{K_{a,\text{input}}}{K_a(1 - \Delta\bar{n})}\right)^{-1} \underbrace{Z_{\text{kin}}(\bar{n} = 0)}_{=1} \tag{5}$$

which finally results in

$$Z_{\text{kin}}(i\Delta\bar{n}) = \prod_{i=1}^{p} \frac{K_a(i\Delta\bar{n})}{K_{a,\text{input}}} \tag{6}$$

for each discrete degree of association $i\Delta\bar{n}$ with i integer values. A closed expression can be derived by introducing the Riemann integral in the thermodynamic limit which yields

$$\ln(Z_{\text{kin}}(i\Delta\bar{n})) = \sum_{i=1}^{i} \ln\left(\frac{K_a(i\Delta\bar{n})}{K_{a,\text{input}}}\right) = N_0 \int_{\Delta\bar{n}\approx0^+}^{i\Delta\bar{n}} \ln\left(\frac{K_a(\bar{n})}{K_{a,\text{input}}}\right) d\bar{n} \tag{7}$$

and which can be further evaluated by using Mathematica[1] to give

$$\ln(Z_{\text{kin}}(x)) = -N_0 \left(x + \ln x + (x-1) \ln \left(\frac{Kx}{c_0(x-1)^2} \right) + \ln \left(\frac{c_0}{K_{\text{a,input}}} \right) \right)_{x=i\Delta\bar{n}} \tag{8}$$

where the last term $\ln(c_0/K_{\text{a,input}})$ represents the lower boundary which finally results in Eqn. (22) in the main article.. Due to the fact that we mostly consider a finite number of titrable groups N_0, we use the above expression instead of the general formula presented in the main article.

One advantage of the analytical expression in Eqn. (19) in the main article is given by the fact that the factor $(\beta P^0 V)^{\bar{\nu}} K \prod_{i=1}^{z} \left[\frac{N_i^0!}{(N_i^0+\nu_i)!} \right]$ which is also present in the transition probabilities can be dropped due to the analytical expression for the kinetic partition sum. Hence, the number of criteria that have to be met are reduced such that the acceptance probability for trial moves is higher.

2 Calculation of the Poisson-Boltzmann heat capacity

Like Naji *et al.*, we identify the configurational internal energy $\int_V d^3 r \frac{\epsilon}{2} [\nabla \Psi(r, T)]^2$ from the Poisson-Boltzmann excess free energy[2]. This expression represents the configurational energy part of the internal potential energy $U_{\text{pot}}(T, V, N)$. One can numerically solve the Poisson-Boltzmann potential Ψ as outlined in Ref. 3. Therefore, the configurational internal energy for two different temperatures T and $T + dT$ can be calculated where the Poisson-Boltzmann equation is solved for these two temperatures independently. Here, it is important to understand that the Manning-Parameter, the Bjerrum length and $\beta = 1/(k_B T)$ are only introduced for convenience, so that the partial derivative with respect to temperature also acts on them. Finally, the numerical derivative $C_{V,\text{pot, PB}} = \frac{\partial U_{\text{pot}}}{\partial T} \approx \frac{U_{\text{pot}}(T+dT,V,N)-U_{\text{pot}}(T,V,N)}{dT}$ can be calculated. The final value of the heat capacity is obtained by adding $3/2 N k_B$ to the the excess part of the heat capacity.

2.1 Analytic Calculation of the Poisson-Boltzmann Heat Capacity

As an alternative to the above described numerical Ansatz to obtain $\frac{\partial U_{\text{pot}}}{\partial T}$, one can use the results by Naji *et al.*[2] in order to obtain the excess heat capacity: First, the average potential energy is identified with

$$\langle E_{\text{pot}} \rangle := \tilde{E}_{\text{PB}} N k_B T, \tag{9}$$

where Naji *et al.* define $\tilde{E}_{\text{PB}}$ in Eqn. (58)[2]:

$$\tilde{E}_{\text{PB}}(\beta_F, \Delta, \xi) := \frac{1}{4\xi} \int_{\tilde{R}}^{\tilde{D}} \tilde{r} \left(\frac{d\Psi}{d\tilde{r}} \right)^2 d\tilde{r} = \frac{1}{\xi} \begin{cases} (1 + \beta_F^2)\Delta + \ln\left[\frac{(\xi-1)^2 - \beta_F^2}{1 - \beta_F^2} \right] + \xi \text{ for } \xi \leq \Lambda_{AF} \\ (1 - \beta_F^2)\Delta + \ln\left[\frac{(\xi-1)^2 + \beta_F^2}{1 + \beta_F^2} \right] + \xi \text{ for } \xi \geq \Lambda_{AF}, \end{cases} \tag{10}$$

where $\Delta = \ln(\frac{D}{R})$ is the lateral extension parameter as described in Ref.[2] and where $\Lambda_{AF} = \frac{\Delta}{1+\Delta}$ is the Alfrey-Fuoss parameter[2]. The parameter β_F is given by the transcendental equation[2,4]:

$$\xi = \begin{cases} \frac{1 - \beta_F^2}{1 - \beta_F \coth(-\beta_F \Delta)} \text{for } \xi \leq \Lambda_{AF} \\ \frac{1 + \beta_F^2}{1 - \beta_F \cot(-\beta_F \Delta)} \text{for } \xi \geq \Lambda_{AF} \end{cases}. \tag{11}$$

Therefore, the transcendental parameter β_F depends on the temperature since it depends on the Manning parameter. Moreover, β_F is only introduced to be able to write down an analytical solution[4], its temperature dependence has to be taken into account in the temperature derivative of the Poisson-Boltzmann configurational internal energy. Therefore, the partial derivative with respect to temperature also acts on the Manning parameter ξ. The heat capacity for the rod-like system can be written as:

$$C_{V,pot} = \frac{\partial \langle E_{\text{pot}} \rangle}{\partial T} = \frac{\partial (\tilde{E}_{\text{PB}} N k_B T)}{\partial T} \quad = N k_B \left[\tilde{E}_{\text{PB}}(\beta_F, \Delta, \xi) + T \frac{\partial (\tilde{E}_{\text{PB}}(\beta_F, \Delta, \xi))}{\partial T} \right] \tag{12}$$

for which β_F and ξ depend on the temperature T and are only introduced for convenience. In fact, both need to be derived with respect to the temperature (Δ is independent of T due

to the fact it is a structural parameter):

$$C_{V,pot} = Nk_B \left[\tilde{E}_{\mathrm{PB}}(\beta_F, \Delta, \xi) + T\frac{\partial(\tilde{E}_{\mathrm{PB}}(\beta_F, \Delta, \xi))}{\partial \beta_F}\frac{\partial \beta_F}{\partial T} + \underbrace{T\frac{\partial(\tilde{E}_{\mathrm{PB}}(\beta_F, \Delta, \xi))}{\partial \xi}\frac{\partial \xi}{\partial T}}_{-\xi\frac{\partial \tilde{E}}{\partial \xi}} \right]. \quad (13)$$

Further, it has to be mentioned that the second term of the formula can be easily calculated since Eqns. (58, 59) by Naji *et al.*[2] provide an expression for $\tilde{E}_{\mathrm{PB}}(\beta_F, \Delta, \xi))$ and $\frac{\partial \beta_F}{\partial T}$ can be calculated via implicit derivation of the transcendental equation (11):

$$\frac{\partial \beta_F}{\partial T} = \begin{cases} \frac{\partial \xi}{\partial T} / \left[\frac{\partial}{\partial \beta_F}\left(\frac{1-\beta_F^2}{1-\beta_F \coth(-\beta_F\Delta)} \right) \right] & \text{for } \xi \leq \Lambda_{AF} \\ \frac{\partial \xi}{\partial T} / \left[\frac{\partial}{\partial \beta_F}\left(\frac{1+\beta_F^2}{1-\beta_F \cot -\beta_F\Delta} \right) \right] & \text{for } \xi \geq \Lambda_{AF} \end{cases} \quad (14)$$

Note that Naji *et al.*[2] do not explicitly mention the second term in the above formula (compare Eqn. (81) in Ref. 2)) since they do not make use of the standard partial derivative. In addition, the partial derivative with respect to ξ is also intended to act on β_F (private communication with A. Naji). Therefore, the above presented expression is formally equal to Eqn. (81) in Ref. 2. All expressions can be evaluated analytically (apart from the determination of β_F) and yield exactly the same heat capacity as in the numerical approach to calculate the Poisson-Boltzmann heat capacity. As a test case, we compared MC simulation results for an electrostatic coupling parameter of around $\Xi = 0.72$ (for the same system, but a different Bjerrum length with $\lambda_B = 0.9\sigma$). In this case, the heat capacity C_V which was obtained from simulations and the Poisson-Boltzmann (PB) prediction are identical with 2% deviation. For higher electrostatic coupling parameters Ξ, the discrepancy between MC/MD simulations and PB increases, however this is anticipated since PB is only strictly valid in the limit $\Xi \to 0$.

3 Counterion Probability Densities

In order to verify the simulations, we also determined the integrated counterion probability density around the rod. For a strongly charged polyelectrolyte the integrated counterion probability density f was previously investigated analytically, for example by Deserno *et al.*[3]. In the Wang-Landau simulations with sampling scheme according to Eqn. (12) in the main article, we checked the integrated counterion probability density for a system with $\bar{n} = 0$. Additionally we performed a canonical simulation for a strongly charged rod and performed the Poisson-Boltzmann calculation for the integrated counterion probability density presented in Ref. 3. The results are shown in Fig. 1 for the system presented in the paper (Bjerrum length $\lambda_B = 2\sigma$). The same system with a smaller Bjerrum length (full
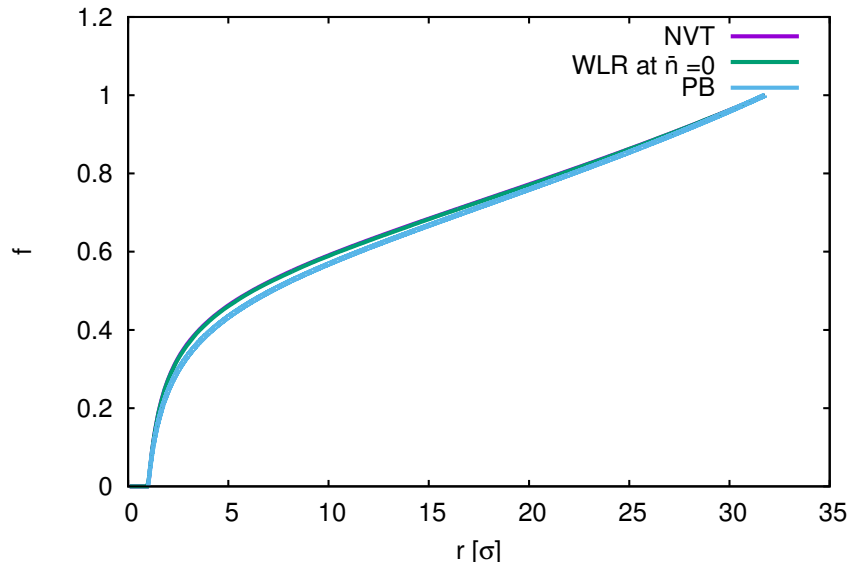

Figure 1: Integrated counterion probability density obtained from PB-Theory, a canonical simulation for the fully dissociated case and from snapshots of the Wang-Landau simulations for $\bar{n} =0$. It is visible that the canonical simulation and the Wang-Landau simulation yield the same counterion distribution.

dissociation, $\lambda_B = 0.9\sigma$ and therefore an electrostatic coupling parameter $\Xi \approx 0.72$) was used to check for the agreement of the PB theory with the canonical simulation. In Fig. 2 the PB integrated counterion probability density and the integrated counterion probability density from the simulations are presented. As one can see there is only very little difference

between the curves. Also the heat capacities C_V differ only by 2% (MC: $C_V/k_B = 36.49+75$, PB: $C_V/k_B = 33.60+75$). Any difference between PB and simulation is expected to decrease further for lower electrostatic coupling parameters.
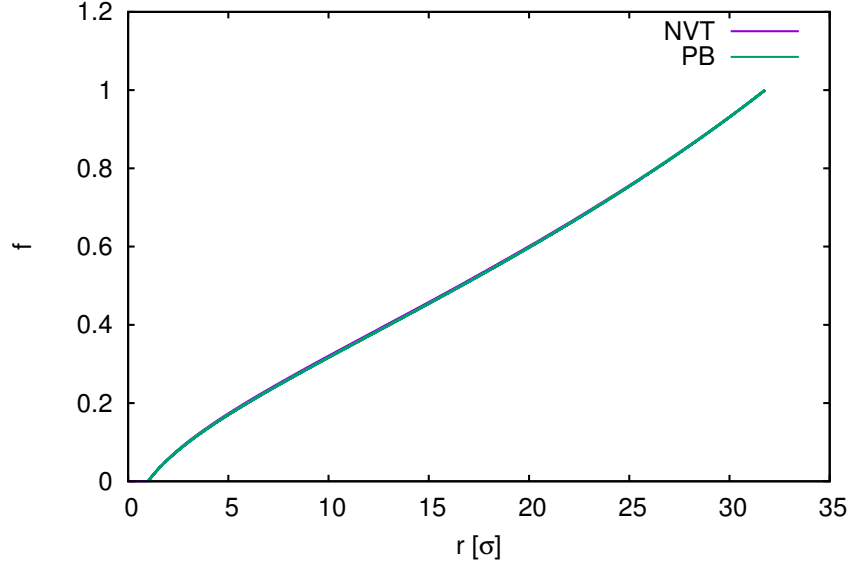

Figure 2: Integrated counterion probability density from PB theory and the results of a canonical simulation for the fully dissociated case at Bjerrum length $\lambda_B = 0.9\sigma$. Simulation data and PB theory are almost indistinguishable.

References

(1) Wolfram, S. *Mathematica: a system for doing mathematics by computer*; Addison Wesley Longman Publishing Co., Inc., 1991.

(2) Naji, A.; Netz, R. R. Scaling and universality in the counterion-condensation transition at charged cylinders. *Phys. Rev. E* **2006**, *73*, 056105.

(3) Deserno, M.; Holm, C.; May, S. Fraction of condensed counterions around a charged rod: Comparison of Poisson-Boltzmann theory and computer simulations. *Macromolecules* **2000**, *33*, 199–206.

(4) Fuoss, R. M.; Katchalsky, A.; Lifson, S. The potential of an infinite rod-like molecule and the distribution of the counter ions. *Proc. Natl. Acad. Sci. USA* **1951**, *37*, 579–589.