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Chapter 1

Report 1

1.1 Simulations Run

1.1.1 Information

Table 1.1 lists the simulations run using n2p2. The things to notice here are the ensemble type and the density(ρ) in the table.

1.1.2 Questions

1. Are we even simulating liquid water at this box size and if we need to reduce the box size/ run an NPT simulation instead?
2. How to decrease box size?

1.1.3 Tentative answers

1. We should reduce the size of the box
2. Using an NPT run - but not sure how to decide pressure

Bias	Ensemble	dt(fs)	Steps	T(K)	N	Box(x,y,z) \AA	ρ (g/cm ³)	outfile
U	NVT	0.5	10,000,000	300	64	46.937,44.121,45.182	0.0204	out_unbiased3.xyz
U	NVT	0.5	100,000	300	64	46.937,44.121,45.182	0.0204	out_unbiased2.xyz

Table 1.1 Simulations for H_2O system using N2P2

Bias column can be decoded from Table 1.2. Not all outfiles may be present on the git repo due to size exceeding 100MB.

Bias	Description
U	Unbiased

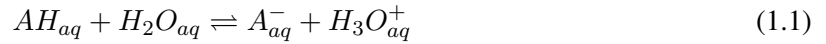
Table 1.2 Description of Bias symbols

1.2 pH calculation

1.2.1 Information [2]

As per Schuurmann et. al [2]:

The dissociation of an acid AH in aqueous solution,



is governed by the equilibrium constant K, which is related to the dissociation constant K_a according to

$$K = \frac{[A_{aq}^-][H_3O_{aq}^+]}{[AH_{aq}][H_2O_{aq}]} = \frac{K_a}{[H_2O_{aq}]} \quad (1.2)$$

(where it is assumed that concentrations can be used instead of activities). The associated free energy change ΔG_{aq} in kilojoules per mole can be written for 1 M solutions at 298 K as

$$\Delta G_{aq} = -2.3RT \log K = 5.71 pK_a + 9.96 \quad (1.3)$$

and correspondingly, the solution-phase dissociation constant pK_a is given by

$$pK_a = 0.175 \Delta G_{aq} - 1.74 \quad (1.4)$$

1.2.2 Information [1]

As per the book Understanding Molecular Simulation From Algorithms to Applications [1]:

In classical statistical mechanics, the Helmholtz free energy F is directly related to the canonical partition function $Q(N,V,T)$:

$$F = -k_B T \ln Q(N, V, T) \equiv -k_B T \ln \left(\frac{\int dp^N dr^N \exp[-\mathcal{H}(p^N, r^N)]}{\Lambda^{dN} N!} \right) \quad (1.5)$$

1.2.3 Free Energy Perturbation (FEP)

As per Jorgensen et. al [3], according to Zwanzig, the free energy difference between an initial (reference) and a final (target) state of a system to an average of a function of their energy difference

evaluated by sampling for the initial state

$$\Delta F = F_1 - F_0 = -\kappa T \ln \left\langle \exp \left(\frac{-(E_1 - E_0)}{\kappa T} \right) \right\rangle \quad (1.6)$$

However, Zwanzig's equation defines E_1 and E_0 as energies of phase space 0 and 1. But, the problem we were trying to solve with free energy was to:

1. Calculate pH using eq 1.4(with corrected constants)
2. Identify phase using Fig 1.1

Hence, there is catch 22 situation.

1.3 Conclusion

I couldn't zero down on a technique to measure individual Gibbs free energy of individual time steps. Infact, from my understanding, gibbs free energy is a macrostate property of a phase space and the inability to define the phase spaces in an unbiased simulation makes us incapable of using eq 1.6. However, replicating the two reaction coordinates in [4] i.e l - number of bonds in a hydrogen wire, ΔE - defined in Figure 1.1, can be used to define phase space and the bias can be used to measure free energy.

1.4 Results

I calculated the free energy difference in consecutive time steps from the first simulation in Table 1.1 using the following formula:

$$\Delta F = F_1 - F_0 = -\kappa T \ln \left(\exp \left(\frac{-(E_1 - E_0)}{\kappa T} \right) \right) \quad (1.7)$$

Note: This is a variation of Zwanzig's equation (eq 1.6) but the average has been replaced with real difference. The results from the first 500 timesteps in plotted in Figure 1.2 (couldn't plot all the frames in a single plot due to memory issues and adding a stride would make the plot pointless)

1.5 What I need help with

1. Is there a way of calculating free energy for an unbiased system that I am unaware of ?
2. What is the mechanism of quenching hydrogen wire protons in figure 1.1 (any leads on that)?

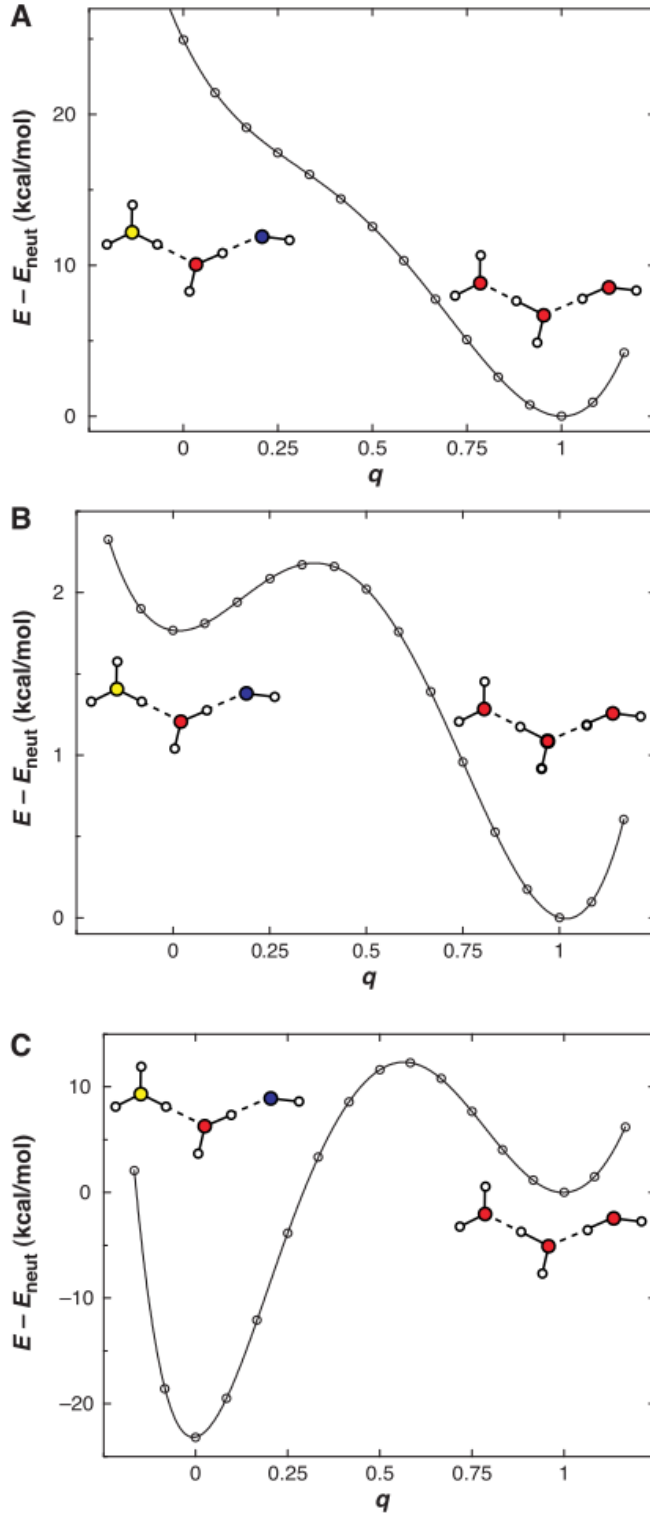


Fig. 2. (A through C) Potential of protons in the hydrogen bond wire connecting hydronium and hydroxide ions. A one-dimensional projection of the $3 \times l$ -dimensional potential is obtained by interpolating between the structures of the two local minima. These minima were determined by quenching wire protons at low temperature while holding all other coordinates fixed. Access to different wells of the potential was provided by moving wire protons artificially, so that ions or neutral molecules were formed. The coordinate q is defined to interpolate between the ionic and neutral configurations, $\mathbf{r}(q) = (1 - q)\mathbf{r}^{(\text{ion})} + q\mathbf{r}^{(\text{neut})}$, where $\mathbf{r}^{(\text{ion})}$ and $\mathbf{r}^{(\text{neut})}$ are the $32 \times 3 \times 3$ -dimensional position vectors specifying the configurations of the entire system in the ionic and neutral minima, respectively. We define the coordinate ΔE as the difference in energy between the two minima, i.e., $\Delta E = E[\mathbf{r}(1)] - E[\mathbf{r}(0)]$, where $E[\mathbf{r}(q)]$ is the energy of configuration $\mathbf{r}(q)$. In (B) and (C), the left minimum (at $q = 0$) corresponds to separated ions. The right minimum (at $q = 1$) corresponds to neutral water molecules. These ionic and neutral structures are labeled in (A), (B), and (C) by schematic wire configurations, with colors as in Fig. 1. The potentials in (B) and (C) were calculated for configurations with $l = 2$, for which the solvent electric field favors separated ions. This electric field is not present in the configuration corresponding to (A). Because the ions are unstable in this case, $\mathbf{r}^{(\text{ion})}$ cannot be obtained by quenching. Instead, it was constructed artificially by moving wire protons to give reasonable ionic structures. All energies are plotted relative to the energy of the neutral minimum, E_{neut} .

Figure 1.1 ΔE reaction coordinate from Geissler paper [4]

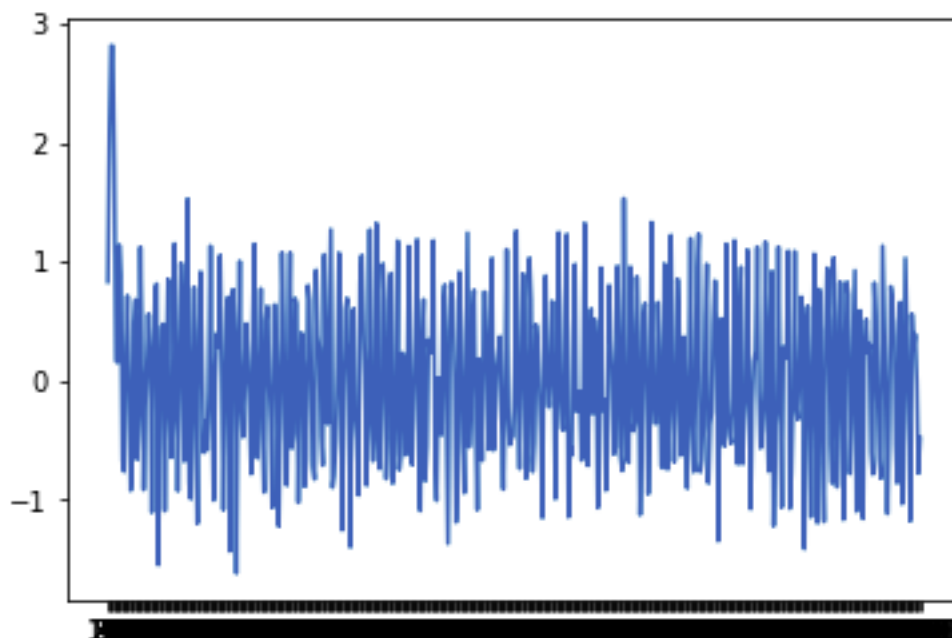


Figure 1.2 ΔF for first 500 timesteps of simulation1 in Table1.1(y axis is in eV and x axis in timestep number)

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