Title: “Chemical work” in statistical mechanics

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Abstract :

In both classical thermodynamics and statistical mechanics entropy plays a crucial role in our understanding of the phase equilibrium and of the reversible and irreversible nature of the macroscopic processes. In this work we will present how to perform direct measurements of the absolute Gibbs free energy and therefore entropy, in molecular systems where the excluded volume restricts the geometrical loci of the accessible phase space. The proposed approach doesn’t require multiple simulation steps as in the case of the traditional thermodynamic integration approach. A molecular “picture” of the “Chemical work” as the work for a process that deletes or inserts particles in the system will be presented in the context of modern non-equilibrium statistical mechanics.

Historically entropy has been introduced by Clausius and since then is essential in our description of both macroscopic and microscopic processes. Whereas classical macroscopic thermodynamics have been formulated based on relating thermodynamic forces to exact and inexact differentials in the macroscopic level, statistical mechanics provide us with a microscopic notion of those quantities in the molecular level.

Herz and Boltzmann related entropy to the microscopic number of states that are compatible with the macroscopic imposed conditions initially described as constants of the dynamical evolution of the microscopic molecular system. For example in a system that does not exchange particle, energy or volume with the environment, the classical Newtonian dynamics preserve energy and momentum, entropy can be rationalize as the logarithm of the number of microstates that are compatible with those conditions.

Whereas the initial attempt to understand the microscopic notion of Entropy was driven by our knowledge of dynamical systems as in the case of Ehrenfest work on adiabatic invariances, it was Gibbs who proposed a statistical ensemble representation capable of linking the microscopic representation and the macroscopic observed classical thermodynamics including open systems where energy and mater can be exchanged. Gibbs formulation of statistical ensembles for open systems where exchanging particles or volume is present, providing us with the statistical mechanical tools to describe phase equilibrium.

Within Gibbs context entropy is a measure of a set. A set of microstates each of which has its one measure, i.e. the Boltzmann weight. As it was shown by Shannon, Gibbs description of entropy can be understood as a comparison of the “amount of information” in the set of the microstates of the ensemble, to the “information” of a random (uninformative) set of microstates.

In this work we will analyze the molecular nature of the chemical work focusing on the entropic contribution that is essential in the phase equilibrium of molecular systems.

We will show that an estimator of the chemical work of adding or removing molecules can be written for any stochastic process that maps the reference and the perturbed system, provided that either the mapping is done properly[1-4].

As in the case of modern non-equilibrium statistical mechanics theory, the chemical work is shown to satisfy the Jarzynski equation[5] and the Crooks fluctuation theorem[6], that relates the probability of observing a value of the mechanical work in the forward and its inverse process.

$$e^{\beta(\Delta \mathrm{A} - \boldsymbol{\mathcal{W}})} P_{Forw}\left(\boldsymbol{\mathcal{W}}_{Forw}\right) = P_{Back}\left(-\boldsymbol{\mathcal{W}}_{Back}\right) \tag{1}$$

We will show how molecular simulation can be used to estimate the chemical work related with the removal of several molecules from the system, in a single perturbation scheme, and that the resulting chemical work distribution will be subject to the central limit theorem and therefore be a Gaussian. By taking advantage of the Gaussian nature of the work distribution, we show that an estimation of the free energy differences between systems of different densities can be constructed based on the estimation of the mean (μ) and the variance (σ^2) of the work distribution, without the need of sampling the tails of the work distribution that would be required in more traditional approaches.

$$\beta \Delta \mathrm{A} = \mu + \frac{1}{2}\sigma^2 \tag{2}$$

Finally the importance of the inaccessible part of the phase space due to the excluded volume of the molecular intermolecular interactions will be addressed in the context of the similarities and differences between chemical and mechanical work.

References

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