



Lessons learned from theory and simulation of step potentials



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ABSTRACT

This article provides a brief review of the model referred to as Step Potentials for Equilibria and Discontinuous Molecular Dynamics (SPEADMD) with observations that may be instructive in formulating the next generation of SAFT models. Effects of branches, fused spheres, rings, and molecular flexibility are demonstrated. The evolution of contributions of the equation of state from low to high molecular weight is shown to be sensitive to details of the molecular structure. Statistical mechanical details are shown to affect the formulation of fundamental theory and trends to be expected. Recent results for contributions beyond second order in temperature are shown to substantially improve predictions in the critical region. For mixtures, it is shown how molecular simulation of the off-lattice excess entropy and energy can be achieved, with implications for mixing rules. A heightened emphasis is placed on the confounded nature of molecular scale site–site interactions relative to macroscopic pure component and mixture data. This leads to general conclusions about how SAFT models should be articulated going forward, and how progress of the thermodynamic modeling community in general might be improved.

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1. Introduction

The SAFT framework has been a tremendous step forward in the formulation of practical equations of state that have a verifiable basis in statistical mechanics and well-defined potential functions. Inevitably, however, discrepancies arise between the original framework (based on flexible, tangent-sphere chains) and more detailed molecular structures and their models. Effects of branches, fused spheres, rings, and flexibility can be demonstrated. To a certain extent, many of these effects have been anticipated through the model referred to as Step Potentials for Equilibria and Discontinuous Molecular Dynamics (SPEADMD). As progress is contemplated to address detailed effects beyond the original SAFT framework, it may be useful to consider the lessons learned from the SPEADMD model. To that end, this article provides a brief review of the SPEADMD model with observations that may be instructive in formulating the next generation of SAFT models.

As engineers apply molecular perspective to the topic of “Fluid Phase Equilibria,” our primary interest is in models of molecular interactions that can be applied to predictions of phase equilibrium and transport properties for engineering applications. This includes phase equilibrium of pure fluids, as characterized by vapor pressure, as well as vapor–liquid equilibria (VLE), liquid–liquid (LLE),

and solid–liquid equilibria (SLE) of mixtures. These kinds of properties have been modeled in the past with equations of state and activity models that are often specific to a particular application. For example, independent UNIFAC models exist for predicting vapor pressure, critical temperature, critical pressure, boiling temperature, vapor–liquid equilibria, and liquid–liquid equilibria. No two of these models share the same UNIFAC parameters. In the context of transferable potential models, all of these properties should be predicted by a single set of parameters. This is an entirely different scale of demand for an engineering model. At first glance, it may seem a “fool’s errand” to attempt such a feat. Nevertheless, we show in the course of this review that predictions of vapor pressure with transferable step potentials are now at a level of outperforming group contribution predictions, naturally subsuming predictions of critical properties and boiling points. Furthermore, predictions of mixed phase equilibria are competitive with existing engineering models. In addition to the practical benefits of having a single general model to predict many properties, there is the pedagogical benefit of relating the macroscopic properties directly to the model of molecular interactions: addressing deficiencies in the macroscopic predictions leads to increasingly sophisticated insights at the nanoscopic level. One might surmise (not over glibly) that knowing the force laws between all atoms would enable chemical engineers to design nanostructures in the same way that civil engineers design infrastructure.

In work occurring over the past 10–15 years, we have

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considered the problem of transferable potential models within the context of discontinuous molecular dynamics (DMD) and thermodynamic perturbation theory (TPT). DMD was necessary because we formulated our potentials as a sequence of steps, as described below. DMD was also convenient because it was much more computationally efficient than MD of continuous potentials (CMD) using the serial processors prevalent at the time. The nature of the DMD algorithm and the basis of its efficiency is discussed in the section on DMD principles. TPT was beneficial because the depths of the steps comprise the perturbations, which are applied post-simulation to infer the entire equation of state $A(T,\rho)$. Through TPT, a specific equation of state is generated for each molecular structure and instance of assumed well-depths, and all of the thermodynamic properties could be computed and compared to experimental data. By minimizing the deviations between computations and experiment, the optimal well-depths could be inferred. We have now characterized the potential functions of roughly 60 site types and 500 molecules [1].

Major components of this transferable potential model were the blister potentials and related theory of associating molecules developed by Wertheim [2]. Note that blister potentials are inherently discontinuous, requiring DMD for simulation of their dynamics from the outset [3]. Noting that the TPT contributions are computed rigorously through the statistical mechanical averages, and the association contribution is computed from Wertheim's theory, our implementation of DMD/TPT is entirely consistent with the spirit of the "statistical associating fluid theory" (SAFT) originated by Chapman et al. [4]. The primary refinements are in the detailed treatment of molecular characteristics such as flexibility, branching, and rings. These details preclude some of the general trends that are often convenient within implementations of SAFT models to date. For example, the local compressibility approximation is not found to be accurate for the second order term, and the perturbation contributions do not scale linearly with a single shape factor applied to the hard sphere reference term. Nevertheless, we consider our model to conform to the SAFT perspective in its most fundamental sense of rigorously connecting assumed potential models with their macroscopic properties. We hope that this review may inform future developers of the SAFT perspective who may be interested in detailed molecular interactions.

The manuscript is organized under three primary headings: pure fluids, mixtures, and databases. The discussion of pure fluids includes mathematical definitions of the manner in which the molecular interactions are characterized through step potentials and their molecular simulations. The quantitative nature of TPT in characterizing the thermodynamics of the full potential is demonstrated and trends in the TPT contributions are analyzed, emphasizing the ways in which molecular details like step depths, softness, flexibility, and branching alter the thermodynamics. The discussion of mixtures shows how molecular simulation leads to functional forms for interpolating simulations with varying composition. These interpolation formulas lead to unambiguous mixing rules at the equation of state level. The consideration of mixtures also leads to emphasis on the site–site nature of molecular interactions and the need for data to characterize these interactions. The discussion of databases addresses the current status and ways that data management can be improved.

2. Fundamentals of DMD/TPT for pure fluids

A number of preliminary considerations must be established before proceeding to review the findings. Among these are basic definitions of the fundamental terms and statistical mechanical averages. The connection between thermodynamic perturbation

theory (TPT) and results of the simulated potential must also be established. These considerations lead to a few observations worthy of special mention in clarifying how step potentials provide a theory that is intermediate between simple square well models and continuous force fields.

2.1. Definition of step potentials and principles of DMD simulation

Step potentials follow a fairly intuitive definition. The potential function is broken down into a sequence of steps that could, in principle, reproduce the square well potential with a single step or the Lennard-Jones potential with roughly a 10–20 steps [5]. The engineering question is how many steps suffice to obtain a potential that represents what can be achieved with a continuous potential? Chapela [5] addressed that question in the context of the single-site Lennard-Jones model. A more general perspective pertains to transferable potential models like n-alkanes. The assumption of transferability involves its own level of approximation. Assumptions inherent in interaction site models for multi-site molecules also involve approximations. Therefore, the answer to this engineering question is not as simple in the context of transferable interaction site models for multi-site molecules. Cui and Elliott addressed this question for n-alkanes and found that four wells were sufficient, with well transitions at $r/\sigma = 1.2, 1.5, 1.8, 2.0$, where r is the site–site center to center distance and σ is the site diameter [6]. Unlu et al. further determined that reasonable accuracy could be retained while reducing the number of parameters by interpolating the middle wells [7]. Since the work of Unlu et al., we have referred to this model of step potentials for equilibria and discontinuous molecular dynamics as the SPEADMD model ("speed-MD").

Table 1 lists samples of the site parameters from the latest characterization [1], and Fig. 1a illustrates a few key site types [7]. One trend is clear at the outset; as a site is located near to other sites such that the ranges of attraction overlap, the optimized potential becomes less steep as the extent of overlap increases. Keep in mind that the potentials are optimized relative to experimental data, the fundamental source of this inference. When we apply potential models with a fixed steepness for all site types (e.g. r^{-6}), we assume a uniform steepness. The r^{-6} dependency was derived for spherically symmetric molecules like argon. It is not clear that it should be exactly the same for overlapping interaction sites, or united atom models. This observation lends added perspective to recent efforts with Mie potentials [8].

We can gain additional insight into the nature of step potentials by considering the attractive overlaps for interaction site models with a square well potential, as illustrated in Fig. 1b [6]. The site diameters, bond lengths, and bond angles are drawn to scale for n-alkanes in the trans conformation. A sample trajectory shows how a probe particle would be deflected as it crosses first one attractive well then another of an ethane molecule. Each of these wells operates independently under the assumptions of interaction site models. The potential energy is double in positions where a single attractive overlap occurs, and triple where double overlaps occur, as in n-butane. Molecules like benzene or neopentane may exhibit triple overlaps. Therefore, a square well potential is actually a multi-step potential when applied as an interaction site model.

Simulations of step potentials are quite different from simulations of continuous potentials. Similar to simulations of hard spheres, the algorithm involves identifying and scheduling collision events. Many of these prospective events never occur, as one site in the list of collision pairs may collide with another partner sooner. Nevertheless, the most efficient means of computation is to sort all prospective events using a binary tree and enable this highly efficient method to identify which event occurs first. In fact, the

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