Fluid Phase Equilibria 425 (2016) 432–442

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

An improved approach for predicting the critical constants of large molecules with Gibbs Ensemble Monte Carlo simulation

Richard A. Messerly, Thomas A. Knotts IV, Richard L. Rowley, W. Vincent Wilding*

Department of Chemical Engineering, Brigham Young University, Provo, UT 84602, United States

ARTICLE INFO

Article history:
Received 6 May 2016
Received in revised form
20 June 2016
Accepted 23 June 2016
Available online 25 June 2016

Keywords:
Molecular simulation
Rackett equation
Experimental design
Uncertainty

ABSTRACT

In this work we focus on predicting the critical temperature (T_c), critical density (ρ_c), and critical pressure (P_c) from Gibbs Ensemble Monte Carlo (GEMC) simulations. Our primary objective is to reduce the uncertainty associated with the critical point constants, particularly P_c, for large molecules. To achieve this goal, we demonstrate the advantages of using the Rackett equation to predict P_c compared to the traditional approach of using the Antoine equation. The main difference is that the Rackett equation utilizes liquid density (ρ_L) while the Antoine equation uses vapor pressure (P_v). The Rackett equation yields a better prediction of P_c than the Antoine equation because ρ_L values are more reliable than P_v values when obtained from GEMC simulations for the standard force field models. As either method will yield large uncertainties in P_c if the uncertainties in ρ_c and/or T_c are large, we also develop a statistically-rigorous experimental design to minimize the uncertainty in T_c, ρ_c, and P_c. The greatest improvement in uncertainty is found for ρ_c and P_c when compared to other contemporary methods.

The critical temperature (T_c), critical density (ρ_c), and critical pressure (P_c) are important thermophysical properties in science and engineering. The critical constants are required to determine equation of state parameters for PVT calculations and to predict other properties based upon the corresponding states principle [1] and other prediction methods. Experimental measurement of critical constants is possible and reliable data exist for a large number of compounds; however, for a number of reasons no experimental data exist for many compounds of interest. For example, obtaining reliable critical constant values becomes difficult for larger compounds because they thermally decompose at temperatures well below T_c. In other cases, the chemical toxicity or reactivity is such that experiments are inadvisable. Situations such as these, where no experimental critical constants are available, render the prediction methods for other properties ineffective for the very molecules for which they are needed.

Due to the importance of the critical properties in engineering practice, multiple groups have made efforts to develop techniques which can obtain the values for molecules that do decompose. For example, the Nikitin group has developed a pulse-heating technique which has permitted experimental measurements of T_c and P_c for n-alkanes as large as C_{60} [2]. However, the P_c values reported by Nikitin et al. for C_{36} differ significantly between their original and more recent publications [3]. This discrepancy is troubling since both the original and more recent values were obtained from the same experimental data and differ only in the data analysis method. In addition, experimental P_c data measured by Teja for n-alkanes up to C_{18} show a strong discontinuity compared with Nikitin's data for larger compounds [4]. Molecular simulation has the potential to help resolve the disagreement but, unfortunately, the existing simulation data found in the literature are not reliable enough to discern between the different experimental data sets.

Historically, predicted critical constant values from Grand Canonical Monte Carlo (GCMC) finite-size scaling methods were considered superior to those obtained from Gibbs Ensemble Monte Carlo (GEMC). There are at least two key limitations to predicting the critical constants with GEMC. First, the GEMC approach suffers from large fluctuations near the critical point. For this reason, it is necessary to perform GEMC simulations at temperatures below T_c and then extrapolate to the critical point. In a previous publication we demonstrated how to rigorously quantify the uncertainty due to extrapolation [5]. In this work, we demonstrate how to reduce this uncertainty. The second supposed limitation is that there is no rigorous approach to correct for finite-size effects with GEMC [6]. However, it was recently shown that finite-size effects for T_c, ρ_c, and P_c are smaller than the corresponding statistical uncertainty for

---

* Corresponding author.
E-mail address: wildingv@byu.edu (W.V. Wilding).

http://dx.doi.org/10.1016/j.fluid.2016.06.041

GEMC systems with 200 molecules of n-decane [7]. These conclusions suggest that GEMC is an attractive option to obtain reliable critical constants because the computational demand is much less than that for GCMC finite-size scaling methods. Unfortunately, the traditional data analysis approach for predicting P_c from GEMC simulation data yields inaccurate results with large statistical uncertainties.

The purpose for the work at hand is to demonstrate an improved approach for estimating the critical constants, particularly P_c, from GEMC simulations. Our main objective is to obtain accurate results with correspondingly small uncertainties. The proposed method is equally rigorous as the approach traditionally found in the literature yet it provides some significant advantages, especially for large compounds, as will be shown.

The proposed methodology is composed of two key aspects. First, as Vetere proposed, we utilize the Rackett equation with liquid density (ρ_L) to more accurately predict P_c [8]. Second, we implement an experimental design to predict the ideal temperatures for the GEMC simulations that will minimize the uncertainty in T_c, ρ_c, and P_c. We show that only two temperatures are needed in the optimal experimental design while most GEMC studies perform simulations at several temperatures. The optimal reduced temperatures (T_R) for performing the GEMC simulations are determined in two different ways. First, a so-called D-optimal experimental design is developed to minimize the uncertainty in T_c, ρ_c, and P_c. A D-optimal design has the advantage that the uncertainties for all three critical constants are reduced simultaneously. Second, a parameter-specific optimization is performed by finding the two temperatures that minimize the variance in just T_c or ρ_c. This approach is ideal in the case where only one critical constant is of interest.

In addition to reducing the statistical uncertainty, we show that this experimental design is less susceptible to finite-size effects which have historically posed a serious limitation for predicting the critical point of large molecules (greater than about C_{26}) [9]. Since this experimental design can reduce uncertainty and finite-size effects without increasing computational time, its use makes GEMC simulation a viable option for studying the thermodynamic behavior of large compounds and should become a valuable tool in this regard.

The outline for this document is the following. In Section 1 we explain the benefits of utilizing Vetere's method for predicting P_c from the Rackett equation and ρ_L simulation data. In Section 2 we explain how the uncertainty in P_c can be rigorously estimated from this method. Then, in Section 3 we demonstrate the need for a D-optimal experimental design to minimize the uncertainty in P_c. In Section 4 the experimental design for GEMC simulations is derived in detail. Next, in Section 5 we present a quantitative comparison of the uncertainties in T_c, ρ_c, and P_c between the experimental design proposed in this work and those found in the literature. This is followed in Section 6 by a brief consideration of modifications to the experimental design, the implications of this experimental design on finite-size effects, and possible limitations of this approach. A step-by-step outline of the proposed methodology is then presented in Section 7. Finally, in Section 8 we discuss our conclusions and the impact they have on predicting the critical constants for large compounds.

1. Alternative method to Predict P_c

A primary reason for the present work is to develop a more effective method for estimating P_c from GEMC simulations of larger compounds. The traditional approach to predicting P_c from GEMC simulation results makes use of the Antoine equation that relates vapor pressure (P_v) to temperature (T) [7]. The form typically used in the simulation literature is

$$\ln(P_v) = A_0 + \frac{A_1}{T} \tag{1}$$

where A_0 and A_1 are fitting parameters. The critical pressure is obtained by first regressing the P_v GEMC data to Equation (1). Then, T_c is obtained by regressing the GEMC results to the law of rectilinear diameters [10] and density scaling law [11]. The law of rectilinear diameters can be expressed as

$$\rho_r \equiv \frac{\rho_L + \rho_v}{2} = \rho_c + A(T_c - T) \tag{2}$$

where ρ_r is the rectilinear density, ρ_v is the vapor density, and A is a fitting parameter. The density scaling law is

$$\rho_s \equiv \rho_L - \rho_v = B(T_c - T)^{\beta} \tag{3}$$

where ρ_s is the scaling density, B is a fitting parameter, and β is a constant, typically 0.326 [7]. Finally, P_c is calculated using T_c and the regression to Equation (1).

The traditional approach for predicting P_c is not ideal for larger compounds for several reasons. The first is that it is very difficult to achieve accurate vapor pressure results from molecular simulation. This is partially due to the fact that P_v is an inherently noisy property when obtained from GEMC simulations. For better statistics, more vapor phase molecules are required which necessitates an increase in the overall number of molecules. However, this comes at a great computational cost for longer chains.

Furthermore, even without increasing the number of molecules in the vapor phase, obtaining P_v becomes computationally intensive for larger molecules because of the "virial" force calculation. The virial forces require an individual calculation for each unique pair of sites in a simulation [12]. Thus, the calculation cost for the virial forces scales as N^2, where N is the number of sites, not the number of molecules. Therefore, assuming the same number of molecules, the computational cost for the virial forces is about 24^2 times more for C_{48} H_{98} than ethane when using a united-atom model. By contrast with Molecular Dynamics, the virial forces are not necessarily computed in Monte Carlo simulations [6]. Therefore, the computationally expensive virial calculation can be completely eliminated by not calculating P_v.

Another reason accurate P_v values are difficult to obtain is because most intermolecular potential model functions, for example the Lennard-Jones 12-6 model (LJ 12-6), do not have the right form to accurately model both ρ_L and P_v [13]. For this reason, most potential models (e.g. OPLS, TraPPE, NERD, etc. [14–16]) are optimized to reproduce ρ_L data. Because the extant models were not designed to yield accurate P_v values the traditional approach for predicting P_c from P_v is inherently limited. On the other hand, the Exponential-6 model developed by Errington et al. [17] and the Mie 16-6 model developed by Potoff et al. [18] are capable of reliably predicting P_v within 3%. Despite this fact, both the Exp-6 and Mie 16-6 models, widely considered two of the best for n-alkanes, show systematic deviations in P_c, especially for larger compounds. This poor performance for P_c is rationalized by Potoff et al. as a "result of compound errors in the predictions of critical temperatures and vapor pressures." In other words, because of the exponential relationship between P_v and T in Equation (1), any deviation or uncertainty in P_v and T_c will be magnified for P_c.

The final limitation of the traditional method is that Equation (1) is often not reliable over a large temperature range. The traditional approach seeks to alleviate this deficiency by obtaining several P_v values at temperatures near T_c. However, since fluctuations in simulation results increase near the critical point this only