

UB association bias algorithm applied to the simulation of hydrogen fluoride

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Abstract

We present a method for accelerating convergence of Monte Carlo (MC) simulations of associating fluids and describe its application to a model for hydrogen fluoride. The new bias scheme preferentially attempts MC trials that lead to unbonding–bonding (UB) transitions of the associating molecules. We apply the algorithm to evaluate properties of the Cournoyer–Jorgensen model of hydrogen fluoride (HF). Superheated vapor properties are calculated from NPT MC simulations over the temperature range of 295.25–318.75 K. Heat capacities and vapor densities are shown. The Gibbs Ensemble technique with UB biasing was used to calculate vapor–liquid coexistence properties over temperatures ranging from 250 to 350 K. Heat of vaporization, coexistence densities and vapor pressures are reported. Simulations performed with no biasing disagree significantly from the UB algorithm data and the new simulations differ also from MC data taken using another biasing algorithm previously developed in our group. The new results coincide better with experimental data taken from the literature for the same state conditions. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

New molecular simulation techniques have allowed simulation of fluids that were not possible in the past. A challenging group of fluids is formed from associating molecules. Strong hydrogen bonding systems represent many of the fluids in this category. Here a short-range, directionally-dependent bond is created by the presence of a highly electronegative atom that interacts with a hydrogen atom. Common examples of industrial importance include simple organic acids, water and hydrogen fluoride (HF).

HF is a favorable candidate for calculation of bulk phase properties via molecular simulation. One reason is the chemically aggressive nature of its fluid phases. Experimental studies, particularly for mixtures, are

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relatively few on account of the danger presented to researchers and cost of special equipment. A further reason is the need to know bulk properties for optimizing processes in which HF plays a significant role, such as production of semiconductors and hydrofluorocarbons. The lack of experimental fluid data can be supplemented with molecular simulation. This is particularly so, given that HF is a small molecule and thus should be amenable to the development of a good molecular model.

In molecular simulations, the strong but short-ranged attractive forces become problematic. Associating fluid phases possess low-energy structures that remain stable in both the liquid and vapor. This clustering phenomenon presents a problem in sampling configuration space because of the unique and comparatively small region that the interaction is most energetic. Consequently, the development of biasing algorithms to treat associating interactions has been a focus of some research. Visco and Kofke applied the monomer addition/subtraction algorithm (MASA) to HF [1]. The method is effective, but its application is limited to chain-forming systems such as HF. Recently, two simple and generally applicable biasing algorithms have been put forth. These are the aggregation volume biasing Monte Carlo (AVBMC) method developed by Chen and Siepmann [2] and the unbonding–bonding (UB) algorithm developed by Wierzchowski and Kofke [3]. The present work demonstrates application of the UB algorithm to vapor–liquid equilibrium and the superheated vapor phase of HF.

Section 2 reviews the UB algorithm and the potential model used in the present simulations, while Section 3 gives results for superheated vapor and VLE coexistence. Finally, conclusions are made about the effectiveness of the UB algorithm for this application.

2. Background

2.1. UB algorithm

A key point in the UB algorithm (as well as AVBMC) is the assignment of an association region to each molecule in the system (or, more precisely, to each molecule participating in the biasing algorithm). The definition of this region is completely arbitrary (except it should not change once the simulation has begun), in that the algorithm can be implemented correctly and with ease regardless of this choice. Of course, the algorithm is most effective if the association region coincides, or at least contains, the region about the molecule where another molecule experiences energetically favorable interactions. This feature of the UB and AVBMC algorithms distinguish them from association-biased algorithms that have preceded this work. In the other methods, the choice of the bias region is usually such that the bias regions on different molecules cannot overlap. In the present approach, overlap of these regions presents no special difficulty and no complex measures are required to account for such a circumstance.

The UB algorithm consists of two moves (unbonding and bonding) that are attempted with equal probability for any Monte Carlo (MC) trial. The unbonding move is initiated by picking one of the $N_{a,i}$ “bound” molecules that are in the association region of another molecule (the terms “bound” and “unbound” are used loosely; there is no chemical binding implied). The move proceeds only if there is at least one molecule bound at the outset of the trial. The molecule is then moved randomly to a point anywhere in the entire simulation region.

Conversely, the bonding move is initiated by picking any molecule at random. The molecule is then moved to a point selected uniformly within the bonding region of one of the remaining molecules, which is selected at random. From the start of the trial there are several ways that the molecule could end up at

Table 1
Probabilities recipe for the unbonding and bonding trial moves

	Unbonding	Bonding
Select move	1/2	1/2
Select molecule i	$1/N_{a,i}$	$1/N$
Select molecule j	–	$1/(N - 1)$
Move molecule	$1/V$	$n_j N / \phi V$

this point and the transition probability of ending up there depends the volume of the biasing region and also the number molecules (n_i) having the point in their biasing region. The scheme can be clearly seen in Table 1.

The unbonding trial results in a probability of

$$T_{ij}^{(U)} = \frac{1}{2} \times \frac{1}{N_{a,i}} \times \frac{1}{V} \times \delta_i \quad (1)$$

where δ_i is zero if the molecule is not bound in state i and one if the molecule is bound. Similarly, the bonding trial probability is

$$T_{ij}^{(B)} = \frac{1}{2} \times \frac{1}{N} \times \frac{1}{N - 1} \times \frac{n_j}{\phi V / N} \quad (2)$$

The probabilities are summed to get a probability of going from state i to state j . According to detailed balance, a final acceptance parameter of

$$\chi = \frac{(N - 1)\phi\delta_j + n_i N_{a,j}}{(N - 1)\phi\delta_i + n_j N_{a,i}} \times \frac{N_{a,i}}{N_{a,j}} \times \exp(-\beta(U_j - U_i)) \quad (3)$$

is given, such that the acceptance probability for the trial is $\min[1, \chi]$.

2.2. Jorgenson potential model

The Cournoyer and Jorgenson (CJ84) potential consists of three point charges and a Lennard–Jones term for the fluorine–fluorine interaction [4].

$$\varepsilon_{mn} = \sum_i^{\text{on } m} \sum_j^{\text{on } n} \frac{q_i q_j e^2}{r_{ij}} + \frac{A}{r_{\text{FF}}^{12}} - \frac{C}{r_{\text{FF}}^6} \quad (4)$$

The A ($3.0 \times 10^5 \text{ kcal } \text{\AA}^{12} \text{ mol}^{-1}$) and C ($425 \text{ kcal } \text{\AA}^6 \text{ mol}^{-1}$) parameters are fit to liquid phase properties along with the gas phase dimer properties. A charge of $q = 0.725e$ is placed on the hydrogen atom and the fluorine atom. A third charge of magnitude $-2q$ is located 0.166 \AA off the fluorine atom towards the hydrogen. The bond radius is fixed at 0.917 \AA .

3. Simulation details

3.1. Bonding region

In applying the UB algorithm to HF, the definition of the bonding region was based on previous studies of the CJ84 potential surface [5]. In light of this, a region was defined to encompass all the energy wells of the potential model. A sphere was placed 2.6 Å off the F atom in the opposite direction of the H atom. The radius of the sphere was set to 4.0 Å. A spherical region centered at the F atom of radius 1.4 Å is excluded from the bonding region (Fig. 1). When a molecule is moved into the bonding region, the H atom is randomly placed within the sphere. The orientation of the moved molecule is chosen at random. The unbonding move proceeds by moving the H atom to a random position in the simulation volume and randomly choosing an orientation.

3.2. Superheated vapor

A NPT MC simulation was performed in the superheated vapor region of HF for a pressure of 96.1 kPa. Three moves (volume, displacement and rotation) in addition to the two biasing moves were conducted on each molecule. Additionally, two choices (selected equally at random) were provided for the displacement and rotation moves. One translation/rotation corresponded to a small move that has a good probability to maintain favorable energetics for bonded molecules; the other permits larger changes, in essence placing the molecule at random in the box or reorienting it to a random position on the sphere. The probability of choosing an unbonding move, a bonding move, a rotation move and a displacement move were equal. Typical simulation procedures, such as periodic boundaries conditions were applied and a target of 50% acceptance for the short-range rotation, short-range trans-

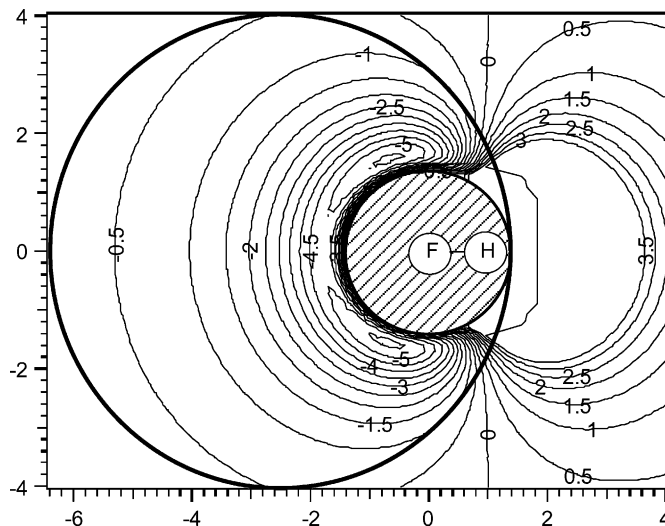


Fig. 1. Contour plot of CJ84 with planar configuration and orientation limited to the HF molecule pointing directly towards the corresponding fluorine atom. The energy is in kcal mol^{-1} and the position is in angstroms. The UB-biased region is indicated by the large circle.

lation and volume move change was implemented by adjustment of the maximum displacement for each move.

The simulations were started from equilibrated configurations for the particular state conditions. One million cycles (where a cycle represents N MC trials) were used for property averaging. The simulated system consisted of $N = 256$ molecules.

3.3. Vapor–liquid equilibrium

The Gibbs ensemble was used to calculate the vapor–liquid equilibrium properties. The system consisted of a total of 512 molecules. Biasing moves were attempted only in the vapor phase. Further, the step size of the translation move and rotation move was only done in the vapor phase. An equilibration period of 500×10^3 cycles was used before averaging. The averaged properties were collect through 500×10^3 cycles.

4. Results and discussion

The densities of the superheated vapor are compared to unbiased simulation results, MASA biasing algorithm results and experimental data [6] in Fig. 2a. Constant-pressure heat capacities are compared to experiment [7] and MASA biasing algorithm results in Fig. 2b.

The superheated vapor densities are significantly larger than those measured in the unbiased and the MASA-biased simulations. Prior results underestimated the experimental data, but the new density data

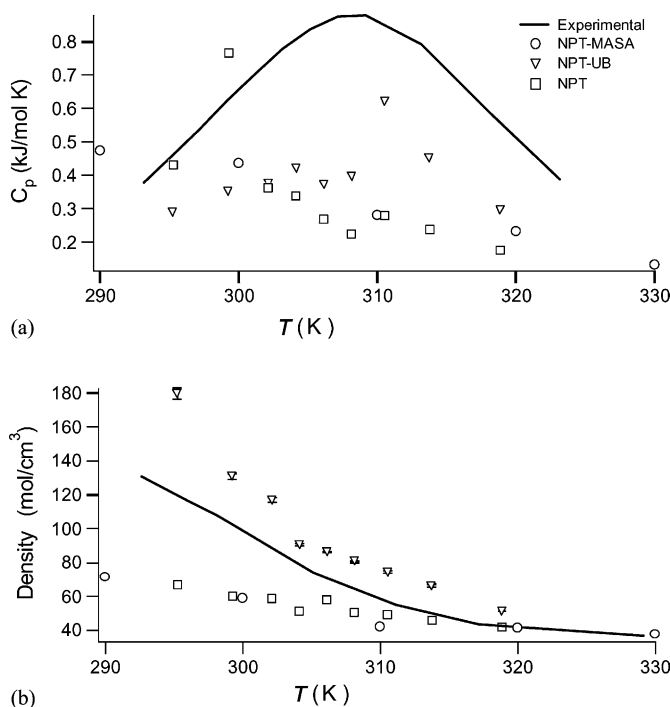


Fig. 2. The heat capacity (a) and density (b) of superheated vapor at 96.1 kPa as calculated from MASA-biased (open circles), non-biased (open squares) and UB-biased NPT simulations for the CJ84 potential model compared to the experimental data [6].

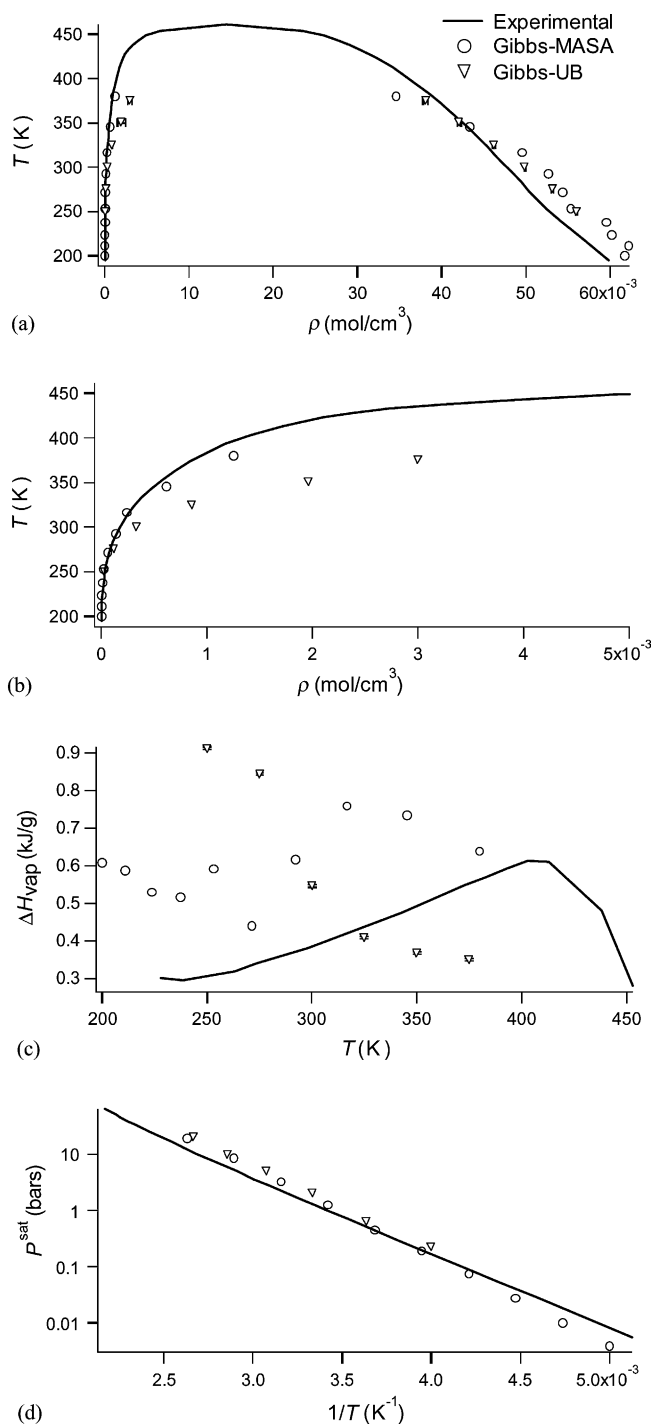


Fig. 3. Coexistence densities (a), saturated-vapor density (b), heat of vaporization (c) and vapor pressure (d) as calculated for the CJ84 potential model from MASA-biased (open circles) and UB-biased simulations (open triangles) compared to experimental data [8].

now exceed the experimental values. The present study has some notable differences from previous studies. The results presented here are for a temperature range consistent with experimental data. The new simulation were conducted for a larger system than in the MASA study and the larger system size enables the sampling of clusters over a broader range of sizes. However, we have not performed a thorough system size study, so we cannot be certain that this effect is relevant. More important, the addition of small-step trial displacements allows for the short-range potential energy surface between a dimer to be sampled more thoroughly. Lower-energy configurations and equilibrium geometries can be found more reliably in the simulation. A simulation without these moves displaces a particle randomly over the entire simulation box. The result is a much higher total energy of the system, which would lead to a lowering of the density.

The corresponding heat capacity data, which are much more difficult to measure with precision as compared to density data, also differ from the earlier results. The new data seem to exhibit a peak in the vicinity of the experimental maximum, although the peak size and shape of the curve differ from experiment. The peak in the heat capacity is connected to the increase in density with decreasing temperature, exhibited by both experiment and the new simulation data. Previous simulation results do not show the same trend in density (or they show it much more weakly) and correspondingly they do not exhibit a heat capacity maximum.

Simulation results for this system using the AVBMC algorithm have been published [2]. The density and heat capacity determined this way are similar to the MASA data over a temperature range between 270 and 330 K. Also, it should be noted the MASA and AVBMC algorithm do not greatly change the properties from the unbiased simulation.

The vapor and liquid densities at equilibrium are given in Fig. 3a and b; the heat of vaporization can be seen in Fig. 3c and vapor pressures are reported in Fig. 3d. The temperature–density curve agrees well with previous simulation data, which are in reasonable agreement with the experimental curve. We have not performed detailed calculations at higher temperatures, but the critical point seems to be underestimated by the model.

The enthalpy of vaporization shows marked deviation from the prior simulation data and both give a poor characterization of the experimental form. The HF system displays an unusual maximum in its heat of vaporization. At lower temperatures cluster formation in the vapor lowers its energy and thereby causes the heat of vaporization to decrease. This trend is displayed by the data, but the peak arises at temperature lower than seen in experiment and takes a different shape. The behavior is consistent with the saturated densities seen in the simulation, which are larger than experiment or the MASA results.

5. Conclusions

Simulation of models for strongly associating systems, such as HF is difficult. We have implemented a biasing algorithm designed to alleviate the sampling problems inherent with this system at low density and we still find it difficult to obtain good results. We think that better results could be obtained with an even tighter association bias, perhaps considering bias of the orientation as well as the position when making bonding trials.

List of symbols

A, C LJ parameters in CJ84
e electrostatic charge

n	number of bonding region molecule resides in
N	total number of molecules
$N_{a,i}$	number of associated molecules
q	charge
r	distance
T	transition probability
U	energy
V	total volume

Greek letters

β	inverse reduced temperature
χ	acceptance parameter
δ	delta function
ϕ	fraction of total volume

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