Thermodynamic Properties of Hydrogen Dissociation Reaction from the Small System Method and Reactive Force Field ReaxFF

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ABSTRACT

We present thermodynamic properties of the H_2 dissociation reaction by means of the Small System Method (SSM) and Reactive force field ReaxFF simulations. Thermodynamic correction factors, partial molar enthalpies and heat capacities of` the reactant and product were obtained in the high temperature range; up to 30000K. The results obtained by ReaxFF potential agree well with previous results obtained with a three body potential (TBP). This indicates that the popular reactive force field method can be well combined with the newly developed SSM for large-scale simulations of chemical reactions. The approach may be useful in the study of heat and mass transport in combination with chemical reactions.

Keywords

Thermodynamics, Small System Method, Hydrogen Dissociation, Reactive force field, Molecular Dynamics

INTRODUCTION

Thermodynamic properties of reactions play a central role in chemistry and chemical engineering. These properties are used to describe macroscopic systems, such as in a laboratory and in chemical reactors. These classical descriptions fail at the nanoscale because thermodynamic variables are no longer extensive for a few particles. Schnell *et al.* [1] have used a *new* scaling law in the development of the Small System Method (SSM), which connects properties of the system in the nanoscale with macroscopic limit. SSM has been successfully used to calculate thermodynamic correction factors (or simply thermodynamic factors), derivatives of activity coefficients with respect to the composition, partial molar enthalpies, partial molar volumes, and reaction enthalpies of macroscopic systems. The results have been in excellent agreement with data obtained from other methods [2]. The calculation of thermodynamic factors (derivative of activity coefficient with respect to composition) or so-called Kirkwood-Buff integrals [3] are of great importance to quantify diffusion. SSM was also applied to find thermodynamic factors for Li^+ ions in solid state conductors [4], alkane in carbon nanotubes [5] and particles in nanopores [6]. The thermodynamic factor allows the calculation of Maxwell-Stefan diffusion coefficients from Fick diffusion coefficients, and vice versa, for binary, even ternary systems [7,8]. Most of these computation studies were

for non-reactive systems. To obtain thermodynamic data in reacting system is of great practical and theoretical importance. Skorpa *et al.* [9,10] studied the H_2 dissociation in equilibrium and under non-equilibrium conditions using a three body potential (TBP) derived from quantum mechanics[11]. They showed the importance of the heat of reaction for the energy transport in a reacting mixture. The presence of the chemical reaction was changing the thermal conductivity as well as the diffusion coefficients. These findings will be of importance for the hydrogen reaction, also at catalyst surfaces such as Pt and Pd. However, the availability of TBP for systems is very limited. The popular reactive force field such as AIREBO[12], ReaxFF [13,14] may then serve as alternatives. The quality and transportability of ReaxFF were dependent on the system and force field optimization[15,16]. An overview of limitation and advantage of this force fields was discussed elsewhere [17]. ReaxFF force field have been successfully applied to many different systems[17], but have not been used together with SSM to calculate thermodynamic properties. In this work, we aim to combine SSM and ReaxFF in order to obtain thermodynamic data for the hydrogen dissociation reaction, to provide a benchmark for further work. We will provide several important properties of this reaction such as the heat capacity, heat of reaction, activation energy and thermodynamic correction factors and compare to values obtained already from the three body interaction potential. With this, we hope to establish how well we will be able to predict the properties of interest.

MODELS AND METHODS

We considered the hydrogen dissociation reaction $H_2 = 2H$. This reaction occurs at a very high temperature. Using computer simulations is a conventional tool to study the reaction. Molecular dynamics (MD) simulations were performed within the LAMMPS package[18]. The parameters used when performing simulations with ReaxFF, were taken from Chenoweth *et al*. [14]. The details of these force fields were given in the literature[14]. We select H_2 system as the first and important step to describe further more complex system. ReaxFF does not have hybridization concept for orbital but based on the bond order to describe the chemical bonding in the system. This approach was proven to be accurately describing a lot of reacting system based on the force field training process [13,14,17]. The simulated system was a cubic box with periodic boundary conditions (PBC) in three dimensions. The box size was in range 28.47 Å to 100 Å, the number of H_2 molecules in the system varied from 37 to 1500. We performed NVT simulation with a step size of 0.1 fs. The system was equilibrated with 1 ns runs at 300K. After that, production runs of another 1 ns were done at higher temperatures in the range of 3639 K - 20796 K to collect and analyze data. The pressure of system was in range of 80-800 bar, which was similar to the conditions of simulation done by Skorpa *et al.* [9]

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As mentioned, when using SSM the thermodynamic properties are calculated from fluctuations in small boxes. The small system can exchange mass and energy with the reservoir. Consequently, the thermodynamic correction factors (TCF) and the partial molar enthalpies as a function of the chemical potentials and the temperature can be calculated from fluctuations of N_i and U. The TCF for a binary mixture with in the grand-canonical ensemble is given by

$$\Gamma_{ij}^{-1} = \frac{1}{\beta} \left(\frac{\partial \ln \langle N_i \rangle}{\partial \mu_j} \right)_{T,V,\mu_{k \neq i}} = \frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N_j \rangle}$$

(1)

Here, $\beta = k_B T$, where k_B is the Boltzmann constant. The dependence of TCF on the size of the small box is found to be approximately linear:

$$\Gamma_{ij}^{-1}(L) = \Gamma_{ij,\infty}^{-1} + \frac{A_{ij}}{L}$$

(2)

We checked the dependence on the size of the reservoir box [2,19]. The partial molar enthalpies in the grand-canonical ensemble can be calculated with SSM using[20]

$$H_i = \left(\frac{\partial H}{\partial N_i} \right)_{T,V,\mu_{j \neq i}} = -\frac{\langle U N_i \rangle - \langle U \rangle \langle N_i \rangle + \langle N_i \rangle k_B T}{\langle N_i^2 \rangle - \langle N_i \rangle^2}$$

(3)

The heat capacity at constant pressure p can be defined as:

$$C_{p,i} = \left(\frac{\partial H_i}{\partial T} \right)_p$$

(4)

The dissociation constant K_X of the reaction (assuming that the gasses are ideal) is

$$K_X = \frac{x_H^2}{x_{H2}}$$

(5)

Where x_i is the mole fraction of molecule i. The standard reaction enthalpy can be found with the van't Hoff equation

$$\frac{d \ln K_x}{d(1/T)} = -\frac{\Delta_r H^0}{R}$$

(6)

The derivative is taken with a constant pressure. The reaction enthalpy is in principle a function of temperature. The dissociation reaction can be assumed to be of first order:

$$-k = \frac{d \ln c_{H2}}{dt}$$

(7)

Where $c_{H2} = N_{H2}/V$ and k (s^{-1}) is the reaction coefficient of the first order reaction. The activation energy can be found using an Arrhenius plot.

$$\ln k_r = \ln A_0 - \frac{E_a}{RT} \qquad (8)$$

RESULTS AND DISCUSSION

Thermodynamic correction factor

We applied the SSM to compute the thermodynamic correction factor in the system with reacting H$_2$ and H-particles. As shown in Fig. 1, at a temperature of 15598K, the value of Γ^{-1} for H$_2$ and H in the system is close to unity. We observed that the value of Γ^{-1} decreases below 0.08Å^{-1} because of the effect of the big box (L). This is in consistent with previous studies[2,21] showing that the Γ^{-1} start dripping when approaching the box limit. The value of $\Gamma^{-1}_{H\text{-}H2}$ is almost zero, indicating no coupling effect between H and H$_2$. This observation agrees well with the previous study using a three-body interaction potential for this system[9].
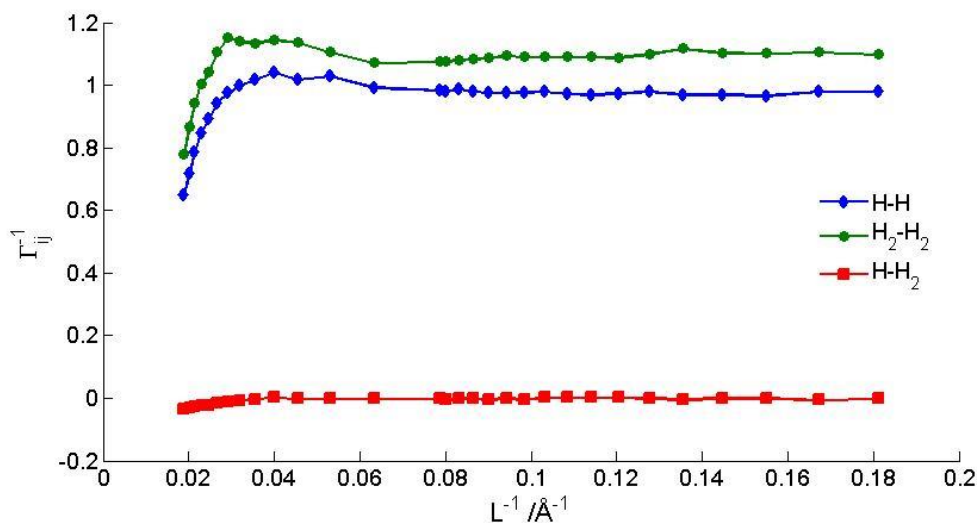

Figure 1. The inverse correction factors (Γ_{ij}^{-1}) as a function of the inverse system length (L^{-1}) at 15597K and at density, ρ=5.22kg/m^3.

We calculate the thermodynamic correction factor (TCF) in the thermodynamic limit, Γ_∞^{-1}, from a linear fit with data taken in the range (L^{-1}: 0.1 and 0.4) similar to previous studies [20,22]. Table 1 presents the TCF at different temperatures obtained by ReaxFF and the TBP potential of Skorpa *et al.* [9]. We found that they are in reasonable agreement with each other. For the case of lower temperature (T=3639K, 7799K), the number of H atom is very low (below 50 atom) because of dissociation reaction is very limited at that

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Table 1: The thermodynamic correction factor at the thermodynamic limit ($\Gamma_{ij,\infty}^{-1}$) . Calculated using different force fields at constant (μ_j,V,T), at density, ρ=5.22kg/m³.

T	ReaxFF			TBP(ref[9])		
	$\Gamma_{HH,\infty}^{-1}$	$\Gamma_{H_2,\infty}^{-1}$	$\Gamma_{H_2H_2,\infty}^{-1}$	$\Gamma_{HH,\infty}^{-1}$	$\Gamma_{H_2,\infty}^{-1}$	$\Gamma_{H_2H_2,\infty}^{-1}$
3639	2.12±0.03	-0.07±0.03	0.945±0.004	1.00	-0.00	0.87
7799	1.14±0.01	0.018±0.005	0.907±0.007	1.00	-0.04	0.91
10398	1.002±0.004	0.025±0.004	1.022±0.006	0.98	-0.08	0.94
12998	0.966±0.003	0.007±0.002	1.023±0.003	0.96	-0.09	0.97
15597	0.965±0.008	-0.007±0.002	1.115±0.007	0.96	-0.12	0.97
20796	0.960±0.005	0.008±0.002	1.14±0.01	0.94	-0.11	0.99

ReaxFF gives values of $\Gamma_{HH2}^{-1,\infty}$ equal to zero within the error bar. We see that the mixture is close to being ideal when the temperature becomes larger than 10 000 K. The van't Hoff equation with constant enthalpy of reaction can be used with greater accuracy for these conditions.

Partial enthalpy and heat capacity

The partial molar enthalpy of each component H_2 and H in the reacting mixture was calculated at different temperatures (Fig. 2). We discovered that the ReaxFF and TBP potentials yield consistently a linear trend in that temperature range. There is a deviation for H_2 molecule at high temperature because of the low number of H_2 molecules at this condition.
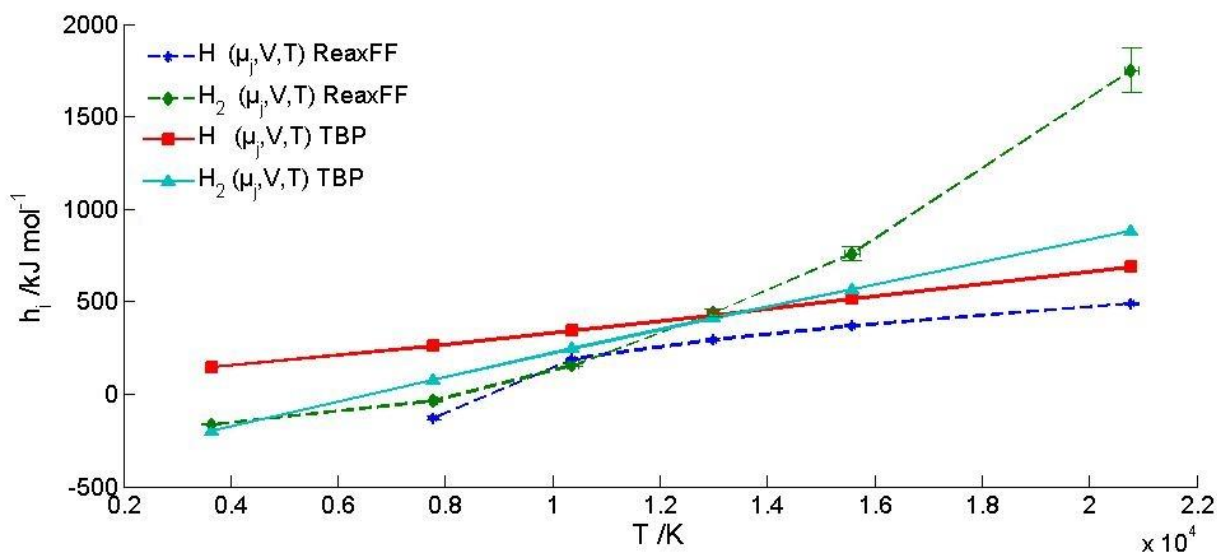
Figure 2. The partial molar enthalpy (h_i) for H and H_2 calculated at different temperatures at constant (μ_j,V,T) and is compared with $h_{i,\infty}$ calculated at the thermodynamic limit with SSM in at constant (μ_j,V,T) with the TBP.

The calculated heat capacity of H and H_2 are tabulated in Table 2. Again, we found results in agreement with results using TBP. The C_p of H_2 molecule is around two times bigger than C_p of H atom in both

scenarios. The results from the ReaxFF and TBP agree within the accuracy of the calculation. The value predicted by ideal gas model underestimates grossly the values obtained with ReaxFF and TBP.

Table 2: The heat capacity of H and H$_2$ with the ReaxFF compared with that of an ideal gas and with the TBP calculations.

	C_{p,H_2} [J/mol K]	$C_{p,H}$ [J/mol K]
ReaxFF (this work)	63±13	28±3
TBP (ref[9,20])	62.8±0.7	31.7±0.7
Ideal gas	37.41	20.75

Reaction enthalpy and activation barrier

Fig. 3 depicts the equilibrium mole fraction of H$_2$ molecule (X_{H2}), and how it varies with temperatures. The profile decreases as expected when the temperature increases. This trend is as expected since the H$_2$ molecule is more dissociated at high temperature. It is very interesting to see that the profile obtained by ReaxFF is in good agreement with that simulated by TBP, see Skorpa *et al*. [9] This indicates that ReaxFF and TBP have comparable quality in the description of the hydrogen dissociation reaction. We applied eq (6) to find the reaction enthalpy ($\Delta_r H$) in the temperature interval from 8000-20796 K, assuming that the activity coefficient ratio is unity. The results are presented in Table 3. The results found by ReaxFF and TBP are in very good agreement. ReaxFF underestimated the ideal value from TBP by 5%. With TBP, also the more accurate equilibrium constant was computed, including the activity coefficient ratio.   We expect that an effort to include this in the ReaxFF calculations, will not change the agreement between the two ways of computation. We also see that the heat capacity of the reaction will be small, as the molecule has almost twice the value of heat capacity of the atom. This explains that the standard reaction enthalpy varies only weakly with the temperature. It was already found [9,20] that its pressure dependence was negligible.
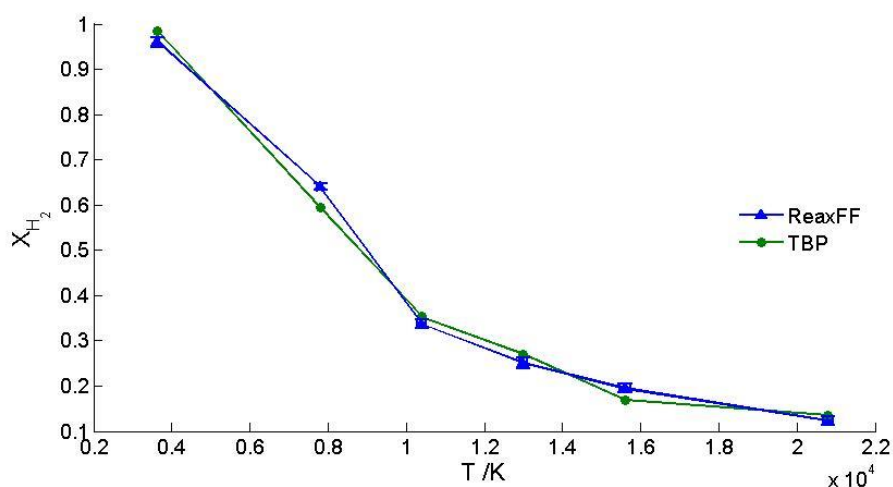

Figure 3 The mole fraction of H$_2$,(X_{H_2}) as a function of temperatures(T) calculated with ReaxFF and compared with results from TBP simulations.

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Table 3: The standard reaction enthalpy of the hydrogen dissociation reaction (Δ_rH), as computed using ReaxFF, assuming that the mixture is ideal.

Parameter	[kJ/mol]
E_a (this work)	438±2
$\Delta_r H^0_{ReaxFF}$ (this work)	302±1
$\Delta_r H^0_{TBP}$ (ref[9]	316±3

We also monitored the conversion of H_2 into H during the simulation time. Fig. 4 shows the time evolution of the number of H_2 molecules, as the reaction proceeds. The profile indicates that the hydrogen dissociation reaction is of first order in the setting with ReaxFF. From the graph, we calculate the reaction kinetic constant as a function of temperature via eq (7) and the activation energy of reaction via eq (8). The activation barrier obtained by ReaxFF via kinetic calculation was not reported earlier by TBP calculation. An activation energy of 438 kJ/mol was found, which is higher than the reaction enthalpy (302 kJ/mol). This indicates that the state of two separate Hydrogen atoms has lower energy than the transition state. In molecular dynamics simulation at high temperature, we are unfortunately not able to monitor the distance between two hydrogen atoms at the transition state. More details of the activated compound on a similar reaction between H and H_2 were described by accurate quantum mechanics calculations[23,24]. The results of reaction enthalpy are comparable for ReaxFF and TBP. However, the activation barrier was not determined in TBP studies [9,20].
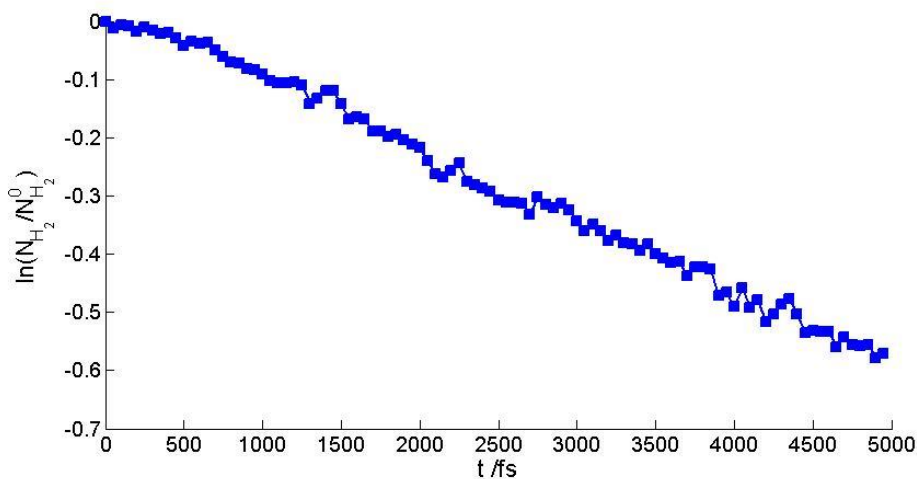
Figure 4. The natural logarithm of the number of H_2 (N_{H_2}) divided by the initial amount ($N_{H_2}^0$) as a function of time (t) at 12998K.

CONCLUSION

We applied the Small System Method to the hydrogen dissociation reaction, using the Reactive force field ReaxFF to provide thermodynamic data, with the purpose of comparing the results from ReaxFF with earlier results with a more accurate interaction potential. The thermodynamic correction factors, heat

capacities, reaction enthalpy and activation energy were reported. The results show that the two ways of computation of thermodynamic data agreed well. The simplifying conditions used in the comparison (ideal mixture approximation) should be kept in mind, however. TBP results seem to be more accurate, but ReaxFF gives the trends and magnitudes we want to see. This opens a possibility to combine SSM and ReaxFF for more complex chemical reactions. This will bring useful information about reactions away from equilibrium, and the mode of heat transport under such conditions.

Acknowledgements

Competing Interests

The authors declare they have no competing interests.

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