

## Direct Monte Carlo simulation methods for nonreacting and reacting systems at fixed total internal energy or enthalpy

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A Monte Carlo computer simulation method is presented for directly performing property predictions for fluid systems at fixed total internal energy,  $U$ , or enthalpy,  $H$ , using a molecular-level system model. The method is applicable to both nonreacting and reacting systems. Potential applications are to (1) adiabatic flash (Joule-Thomson expansion) calculations for nonreacting pure fluids and mixtures at fixed  $(H, P)$ , where  $P$  is the pressure; and (2) adiabatic (flame-temperature) calculations at fixed  $(U, V)$  or  $(H, P)$ , where  $V$  is the system volume. The details of the method are presented. The method is compared with existing related simulation methodologies for nonreacting systems, one of which addresses the problem involving fixing portions of  $U$  or of  $H$ , and one of which solves the problem at fixed  $H$  considered here by means of an indirect approach. We illustrate the method by an adiabatic calculation involving the ammonia synthesis reaction.

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Calculations of the properties of fluid systems using a molecular-based model at fixed total internal energy,  $U$ , or at fixed total enthalpy,  $H$ , are important problems of both theoretical and practical interest. Two examples are (1) adiabatic flash (Joule-Thomson expansion) calculations for nonreacting pure fluids and for mixtures at fixed  $(H, P)$ , where  $P$  is the pressure, and (2) adiabatic flame-temperature calculations for reacting mixtures at either fixed  $(U, V)$ , where  $V$  is the system volume, or at fixed  $(H, P)$ . For such problems a main objective is to calculate the system (absolute) temperature  $T$  and other system properties.

In this paper, we describe a methodology for performing Monte Carlo simulations at fixed  $U$  or at fixed  $H$ , for both nonreacting and reacting systems. The resulting methods enable the direct solution of such problems. We compare our approach with existing related simulation methodologies for nonreacting systems, one of which addresses a different problem of fixing portions of  $U$  or of  $H$ , and one of which solves the problem at fixed  $H$  considered here by means of an indirect approach. For reacting systems (not considered by existing methods), we describe how to implement in conjunction with our approach the reaction-ensemble Monte Carlo method (REMC) [1]. To illustrate our methodology, we provide an example of an adiabatic calculation involving the ammonia synthesis reacting system using a molecular-based model.

### I. SIMULATIONS AT FIXED $U$ AND FIXED $H$

We consider the independent variables of a Monte Carlo canonical-ensemble simulation as the set  $\{N_i, V, \beta\}$ , where  $N_i$  is the number of particles of species  $i$ ,  $\beta = 1/(kT)$ , and  $k$  is

Boltzmann's constant. The dependent variable is the dimensionless Helmholtz energy,  $\beta A$ . The goal is to perform a simulation at a specified value of  $\partial(\beta A)/\partial x$ , where  $x$  is one of  $\{N_i, V, \beta\}$ ; these derivatives are given by  $\partial(\beta A)/\partial N_i = \beta \mu_i$  (where  $\mu_i$  is the chemical potential of species  $i$ ),  $\partial(\beta A)/\partial V = -\beta P$  and  $\partial(\beta A)/\partial \beta = U$ . Although simulation methods implementing constant values of the first two derivatives are well known [2], we consider all three cases from the same viewpoint to obtain the proposed approach.

The proposed method involves combination of the usual particle displacement moves during an  $(N_i, V, \beta)$  simulation with moves to fix the specified value of the derivative,  $\partial(\beta A)/\partial x$ , where  $x$  is a member of the set  $\{N_i, V, \beta\}$ . In order to obtain the appropriate acceptance probability for changes in the variable  $x$  ( $x$  moves,  $\Delta x$ ), we employ methodology similar in spirit to that used by the virtual-parameter-variation approach for calculating  $\partial(\beta A)/\partial x$  in a simulation [3]. Here, we consider solving the problem at hand as a strategy for solving the nonlinear equation

$$\frac{\partial f}{\partial x} - d = 0 \quad (1)$$

for  $x$ , where  $f \equiv \beta A$  and  $d$  is the specified value of the derivative. This is equivalent to solving the equation

$$\left\langle \exp\left(\frac{\partial f}{\partial x} - d\right) \right\rangle = 1, \quad (2)$$

where the angular brackets denote a canonical-ensemble simulation average.

We assume there is a unique solution to Eq. (1), and consider the two cases when  $f$  is either strictly convex or strictly concave with respect to  $x$ . When  $f$  is convex, solving Eq. (1) corresponds to *minimizing*  $F(x)$  with respect to  $x$ , where

$$F(x) = f(x) - dx. \quad (3)$$

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In this case, the acceptance probability for a change  $\Delta x$  involving Eq. (2) is

$$\begin{aligned} \mathcal{P}_{\text{convex}}(\Delta x) &= \min[1, \exp(-\Delta F)] \\ &= \min\left\{1, \exp\left[-\left(\left(\frac{\partial f}{\partial x}\right)_0 - d\right)\Delta x\right]\right\}, \end{aligned} \quad (4)$$

where the subscript 0 denotes the current simulation value. When  $f$  is concave, solving Eq. (1) corresponds to *maximizing*  $F(x)$ , or equivalently to *minimizing*  $-F(x)$ . The acceptance probability for a change  $\Delta x$  involving Eq. (2) in this case is

$$\begin{aligned} \mathcal{P}_{\text{concave}}(\Delta x) &= \min[1, \exp(\Delta F)] \\ &= \min\left\{1, \exp\left[\left(\left(\frac{\partial f}{\partial x}\right)_0 - d\right)\Delta x\right]\right\}. \end{aligned} \quad (5)$$

$\beta A$  is a convex function of  $N_i$  and  $V$ , due to the material and mechanical stability conditions, respectively [4], and the resulting acceptance probabilities for implementing simulations at constant  $x \equiv \mu_i$  and at constant  $x \equiv P$  match the known results [2]. Unlike the situation for the first two variables,  $\beta A$  is a *concave* function of  $\beta$ , due to the thermal stability condition [4], and for a simulation at constant specified total internal energy, i.e., at fixed  $(N_i, V, U)$ , we must use Eq. (5). We set

$$U = U^{\text{IG}} + \mathcal{U}, \quad (6)$$

where IG denotes the ideal-gas value, and  $\mathcal{U}$  is the configurational energy. The acceptance probability for a change  $\Delta\beta$  is then

$$\mathcal{P}(\Delta\beta)^{\{U, V\}} = \min\{1, \exp[(U_0^{\text{IG}} + \mathcal{U}_0 - U^*)\Delta\beta]\}, \quad (7)$$

where the superscript \* denotes the specified value.

For a simulation at fixed  $(N_i, P, H)$ , we set

$$\begin{aligned} f &= \beta A + \beta P V \equiv \beta G, \\ \frac{\partial f}{\partial \beta} &= U + P V \equiv H = H^{\text{IG}} + \mathcal{U} + P V - \frac{N}{\beta}, \end{aligned} \quad (8)$$

where  $G$  is the Gibbs energy and  $N$  is the total number of particles in the system. Since  $\beta G$  is a concave function of  $\beta$ , Eq. (5) gives the transition probability for a change  $\Delta\beta$  as

$$\begin{aligned} \mathcal{P}(\Delta\beta)^{\{H, P\}} \\ &= \min\left\{1, \exp\left[\left(H_0^{\text{IG}} + \mathcal{U}_0 + P^* V_0 - \frac{N}{\beta_0} - H^*\right)\Delta\beta\right]\right\}. \end{aligned} \quad (9)$$

In the above, the IG values are conveniently obtained from tabular compilations of thermochemical data [5] and the definitions

$$H^{\text{IG}} = \sum_i \frac{N_i}{N_A} h_i^{\text{IG}}, \quad (10)$$

$$h_i^{\text{IG}} = \Delta H_{fi}(298.15) + \int_{298.15}^T c_{P_i}(T) dT, \quad (11)$$

$$U^{\text{IG}} = H^{\text{IG}} - NkT, \quad (12)$$

where  $\Delta H_{fi}$  is the molar enthalpy of formation of species  $i$ ,  $c_{P_i}$  is its molar heat capacity, and  $N_A$  is Avogadro's constant.

Simulations at specified  $(N_i, V, U)$  and  $(N_i, P, H)$  thus entail simulations in the  $(N_i, V, \beta)$  ensemble involving  $\beta$  change moves with transition probabilities given, respectively, by Eqs. (7) and (9), in addition to the usual particle translational and rotational moves, and volume change moves to fix  $P$  if appropriate. Finally, if chemical reactions occur in the system, they may be implemented by including reaction moves via the REMC methodology [1].

## II. COMPARISON WITH EXISTING SIMULATION METHODS FOR NONREACTING SYSTEMS

Ray and Graben [6] developed approaches for performing a simulation at a specified value of the sum of the system kinetic energy and the configurational energy, and at a specified value of the sum of these quantities and  $PV$ . The system kinetic energy corresponds to  $(f/2)N/\beta$ , where  $f$  is the number of degrees of freedom per particle. The specified quantities do *not* correspond to the total internal energy and total enthalpy, respectively, since electronic energy-level contributions to  $U^{\text{IG}}$  in the case atomic fluids, and vibrational and electronic energy-level contributions to  $U^{\text{IG}}$  in the case of molecular fluids are *not* included (rotational energy levels are treated approximately). Kristóf and Liszi [7] used the approach of Ray and Graben to formulate an alternative Gibbs-ensemble method for calculating vapor-liquid equilibria, a different problem from that considered here.

Escobedo and Chen [8] developed a method based on thermodynamic integration for calculating the properties of pure fluids and mixtures at fixed  $H$  (in principle, a similar approach could be implemented at fixed  $U$ ), using

$$\left(\frac{dT}{dP}\right)_H = \frac{N}{N_A c_P} \left[ T \left(\frac{\partial V}{\partial T}\right)_P - V \right]. \quad (13)$$

This approach can be used to perform an  $(H, P)$  calculation, but it requires integration from an initial state  $(T_0, P_0)$  defining  $H$ , involving a sequence of simulations to calculate the integrand of Eq. (13) at intermediate state points.

## III. EXAMPLE: ADIABATIC SIMULATION OF AMMONIA SYNTHESIS REACTION

As an illustrative example of our methodology, we consider ammonia synthesis



in an adiabatic flow reactor, with the inlet stream consisting of a stoichiometric feed of  $\text{N}_2$  and  $\text{H}_2$  at the temperature  $T_{in} = 298.15$  K and the pressure  $P = 1000$  bars, corresponding to an inlet enthalpy,  $H_{in}$ . The adiabatic reaction tempera-

ture occurs at the reactor exit when the exit stream is at reaction equilibrium and the value of the total enthalpy at the exit is unchanged from that at the inlet,  $H_{ex} = H_{in}$  [9].

We modeled nitrogen as a two-site Lennard-Jones (LJ) molecule with the addition of three point charges to account for its quadrupole, using the molecular interaction parameters of Vrabec *et al.* [10]. The hydrogen molecule was modeled as a single LJ sphere with the addition of three point charges to account for its quadrupole, using the molecular interaction parameters of Darkrim and Levesque [11]. For ammonia, the model of Gao *et al.* [12] was used, consisting of a LJ plus negative point-charge site to represent the nitrogen atom, and three positive point charges to represent the three hydrogen atoms. The IG quantities involved in Eqs. (9) to (12) were taken from the JANAF thermochemical tables [5] and the simulations were performed using 500–1000 molecules.

We first carried out a simulation at constant  $(N_i, P, \beta)$  of a system corresponding to the inlet  $N_2/H_2$  mixture to deter-

mine the value of the enthalpy  $H_{in}$ , calculating it *via* Eq. (8). We then carried out a combined  $(H, P)$  and REMC simulation at this value of  $H$ .

The inlet stream enthalpy was determined as  $0.8861 \pm 0.0081$  kJ mol<sup>-1</sup>, and the exit temperature was calculated to be  $T_{ex} = 850.9 \pm 1.5$  K. The exit mole fractions were  $y(N_2) = 0.146 \pm 0.001$ ,  $y(H_2) = 0.438 \pm 0.001$ , and  $y(NH_3) = 0.416 \pm 0.002$ . The importance of the nonideality contributions is illustrated by the fact that adiabatic calculations involving an ideal-gas model yield an exit temperature of 798.5 K, exit mole fractions  $y(N_2) = 0.155$ ,  $y(H_2) = 0.465$ , and  $y(NH_3) = 0.380$ .

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