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Molecular simulation of the enthalpies of argon (1) + methane (2) at different temperatures and pressures

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Abstract

The Gibbs-ensemble Monte Carlo simulation method was applied to calculate the enthalpies of the argon (1) + methane (2) system at 150.72 and 164.0 K. The Lennard-Jones (LJ) potential function was adopted to describe the intermolecular interactions. Three hundred spherical, isotropic particles were used in all simulation runs. A new particle transfer method is proposed that has been found to be more efficient than the random insertion method. A satisfactory agreement was obtained between our simulation results and the predictions by the Soave and Peng–Robinson equations of state (EOSs).

INTRODUCTION

In recent years, molecular simulation methods for the prediction of basic thermodynamic and structural properties of fluids have seen significant advances. Great efforts have also been made in improving the efficiency of simulation techniques for the estimation of free energies [1–4] in order to predict the phase equilibria of model and real fluids.

Such traditional methods as the test particle method [5], the grand canonical ensemble [6], the semi-grand canonical ensemble [7, 8] and thermodynamic integration [9] can be used to perform simulations at different densities and compositions; the coexisting phases satisfying the Gibbs equilibration conditions can be determined through interpolation [2, 10]. Obviously, these methods share the disadvantage of being time-consuming. Therefore, most previous simulation studies have been restricted to uniphase systems.

Panagiotopoulos and co-workers [11, 12] have devised a so-called

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"Gibbs-ensemble Monte Carlo simulation methodology." With its advantage of not needing to evalute the chemical potentials of the components, this method is a powerful tool in computer simulation studies. But, like traditional methods, this simulation technique has great difficulty in treating high-density phases. In this work, we propose a novel insertion method to overcome partially this limitation. We have also applied this technique to simulate the enthalpies of argon (1) + methane (2) at 150.72 and 164.0 K, and comparisons are made between simulation results and the predictions of EOSs.

COMPUTATIONAL PROCEDURE

In this paper, all simulations were performed with 300 particles. Each run started from a face-centered cubic (fcc) lattice configuration, and each box contained 150 molecules at the very beginning.

In order to meet the criteria of phase equilibration, we have perturbed, in cycles, the simulation system according to the following sequence.

(A) Molecular displacement

Molecules in the two regions were moved in turn with an acceptance probability of p_d where

$$p_d = \min\{1, \exp[-\beta(\Delta U^{\alpha} + \Delta U^{\gamma})]\} \tag{1}$$

where $\beta = (kT)^{-1}$ and ΔU is the energy difference due to the position perturbation of a molecule.

(B) Volume rearrangement

After 500 trials of molecular displacement, a random volume change was made to a randomly selected region (e.g. phase α), and the trial configuration occured with probability p_v

$$p_v = \min\left\{1, \exp\left[-\beta(\Delta U^{\alpha} + P\Delta Y^{\alpha})N^{\alpha} \ln \frac{V^{\alpha} + \Delta V^{\alpha}}{V^{\alpha}}\right]\right\} \tag{2}$$

where ΔV is the volume change and P the experimental pressure.

(C) Molecular transfer

In this step, 150 attempts of particle interchange were made. With equal probability, we chose at random the receiving box (e.g. phase α, then phase

γ became the supplying one), and also the identity, e.g. A, of a species to be exchanged. The trial move is accepted with the following probability:

$$p_t = \min\left\{1, \exp\left[-\beta\left(\Delta U^\alpha + \Delta U^\gamma + kT \ln \frac{V^\gamma(N_A^\alpha + 1)}{V^\alpha N_A^\gamma}\right)\right]\right\} \tag{3}$$

where ΔU^α and ΔU^γ are the energy changes of phases α and γ due to the creation and destruction of a molecule of species A, respectively.

In simulation runs, we took the cutoff radius (r) to be half the box side-length (L). The long-range corrections (LRC) to thermodynamic properties were integrated with the assumption of $g(r) = 1.0$ for $r > r_c = 0.5L$. In step (B), the scaling technique was adopted to simplify the calculation of energy, pressure, enthalpy and LRC. In the computer program, periodic boundary conditions (PBC), spherical cutoff and minimum image convention were applied. The configurational energy was assumed to be pair-wise additive.

A NEW MOLECULAR TRANSFER TECHNIQUE

From the statistical point of view, the microscopic structures of fluid molecules have coordination shells as a result of intermolecular interactions. This characteristic appears in the form of periodic peaks and valleys in the curve of radial distribution function (RDF) versus distance (Fig. 1).

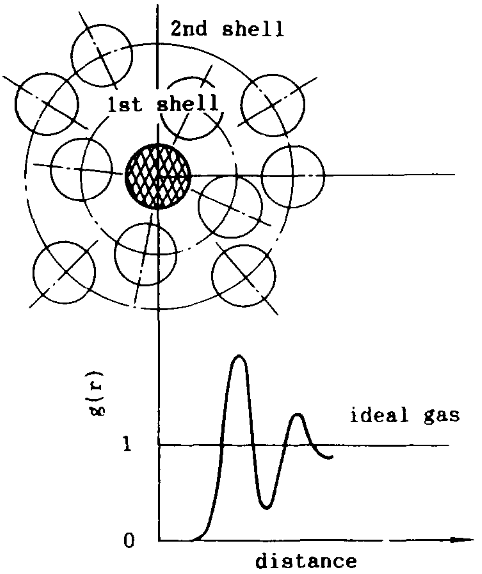

Fig. 1. Coordination shells and radial distribution function.

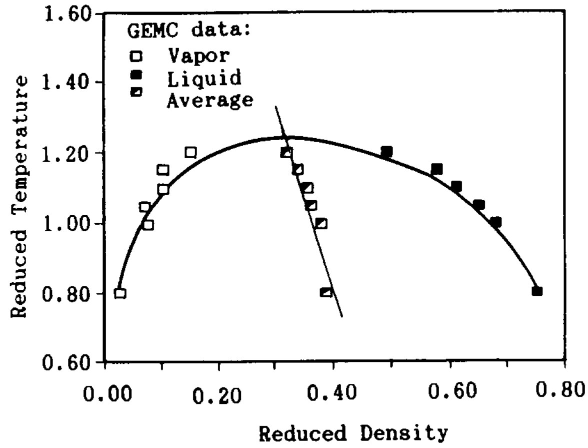

Fig. 2. Coexistence curve of pure square-well fluids.

The peaks and valleys correspond to the molecular layer and hollow ring, respectively. Therefore, it is likely that the successful possibility of a transfer attempt is increased by putting a test particle onto a randomly selected position within the valley region between the first and second coordination shells.

For pure square-well (SW) fluids, the simulation result showed an increase in acceptance ratio of nearly 30% at $T^* = 1.0$. Figure 2 represents the coexistence curve of pure SW fluids [13].

PROGRAM CHECK

To examine the validity of our progam, we have simulated the phase equilibria of a binary LJ fluid with $\varepsilon_{11} = \varepsilon_{22} = 1.0$, $\varepsilon_{12} = \varepsilon_{21} = 0.75$, and $\sigma_{11} = \sigma_{22} = \sigma_{12} = \sigma_{21} = 1.0$ at $T^* = 1.15$ and $P^* = 0.098$. For pure LJ fluids, we have performed simulation at two reduced temperatures, $T^* = 1.0$ and 1.15. The results are listed in Tables 1 and 2. For comparison, the simulated data of Panagiotopoulos et al. [12] are also included. They are clearly in

TABLE 1

Simulated results of vapor–liquid equilibria for an LJ mixture [a]

	x_1	y_1	P_V^*	P_L^*	ρ_V^*	ρ_L^*	$-U_V^*$	$-U_L^*$	N
This work	0.254	0.364	0.095	0.106	0.145	0.484	0.985	3.038	300
Ref. 12	0.261	0.356	0.100	0.105	0.199	0.510	-	-	600
	(±0.013)	(±0.024)	(±0.010)	(±0.018)	(±0.058)	(±0.023)			

[a] The reduced quantities are defined as: $P^* = P\sigma_{11}^3/\varepsilon_{11}$, $\rho^* = (N/V)\sigma_{11}^3$, $U^* = U/(N\varepsilon_{11})$, where N is the total molecular number in the phase and V the volume of the box.

TABLE 2

Coexistence properties of pure LJ fluids[a]

	T^*	ρ_V^*	ρ_L^*	P_V^*	P_L^*	$-U_V^*$	$-U_L^*$
This work	1.0	0.031	0.708	0.027	0.018	0.285	4.93
		(±0.005)	(±0.001)	(±0.003)	(±0.027)	(±0.021)	(±0.01)
Ref. 12		0.029	0.702	0.025	0.024	0.275	4.90
		(±0.001)	(±0.006)	(±0.001)	(±0.027)	(±0.018)	(±0.03)
This work	1.15	0.080	0.605	0.067	0.078	0.674	4.15
Ref. 12		0.083	0.612	0.064	0.075	0.712	4.20
		(±0.006)	(±0.009)	(±0.005)	(±0.024)	(±0.018	(±0.06)

[a] The reduced quantities are defined as: $T^* = kT/\varepsilon_{11}$, $P^* = P\sigma_{11}^3/\varepsilon_{11}$, $\rho^* = (N/V)\sigma_{11}^3$ and $U^* = U/(N\varepsilon_{11})$, where N is the total molecular number in the phase and V the volume of the box.

good agreement, indicating that our simulation program is correct and reliable.

SIMULATION OF ENTHALPY

We considered both argon and methane as spherical, isotropic molecules, and applied LJ potential to describe their intermolecular interactions:

$$u_{ij}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \tag{4}$$

The optimized molecular parameters are listed in Table 3.

For simple monatomic, non-polar fluids, it is reasonable to use the most common mixing rules for both the energy and size parameters

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{0.5} \quad \text{(Berthelot)} \tag{5}$$

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad \text{(Lorenz)} \tag{6}$$

We have simulated the enthalpies of this mixture at 150.72 and 164.0 K;

TABLE 3

Optimized potential parameters used [14]

Substance	ε_{ii}/k (K)	σ_{ii} (Å)
A_r (1)	117.5	3.390
CH_4 (2)	147.9	3.730

TABLE 4

Comparison of the enthalpies of Ar (1) + CH_4 (2) from the Monte Carlo simulation results and from the EOS predictions

P (bar)	$-\Delta H_v$ (kJ mol^{-1})			$-\Delta H_L$ (kJ mol^{-1})		
	MC	Soave	PR	MC	Soave	PR
$T = 150.72$ K						
15.0	0.706(30)	0.736	0.759	6.669(112)	7.012	7.067
20.0	0.956(71)	0.887	0.912	6.240(120)	6.548	6.597
25.0	0.926(73)	1.063	1.091	5.937(116)	6.108	6.152
30.0	1.108(93)	1.279	1.311	5.670(156)	5.639	5.677
38.0	1.357(75)	1.712	1.754	4.975(62)	4.828	4.860
$T = 164.0$ K						
22.879	1.061(55)	1.130	1.163	6.363(108)	6.442	6.494
26.182	1.304(95)	1.243	1.277	6.135(115)	6.204	6.252
27.358	1.234(74)	1.292	1.326	6.049(111)	6.140	6.186
30.691	1.446(93)	1.421	1.455	5.783(218)	5.907	5.959
35.139	1.645(130)	1.611	1.644	5.760(110)	5.559	5.595
38.969	1.775(184)	1.825	1.858	5.447(248)	5.292	5.321
42.090	2.311(91)	2.028	2.058	5.272(133)	5.035	5.057
45.049	2.156(350)	2.253	2.275	5.213(134)	4.788	4.801
48.757	2.384(553)	2.946	2.901	4.452(425)	4.465	4.459
50.986	4.641(326)	3.981	3.943	4.806(166)	4.297	4.275

the results are shown in Table 4 where the statistical errors were obtained by taking ensemble averages over several subsets of Markov chain, excluding the equilibration length of 4×10^5 configurations. To compare these with the traditional methods, we also include the correlation results of the Soave [15] and PR [16] equations of state. Both the energy and co-volume parameters in the EOSs were combined with quadratic mixing rules

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{7}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{8}$$

The combining rule for cross parameters yields

$$a_{ij} = (1 - k_{ij})(a_{ii} a_{jj})^{0.5} \tag{9}$$

$$b_{ij} = (b_{ii} + b_{jj})/2 \tag{10}$$

Figure 3 depicts a comparison of the enthalpy obtained from the simulated data and from the PR-EOS calculation results. Figure 4 is the fluctuation chart of the mole fractions of the vapor and liquid phases,

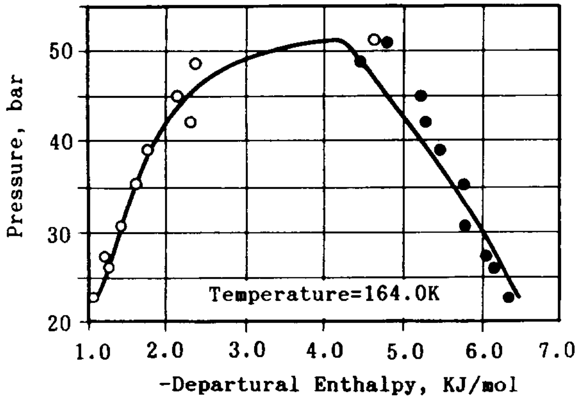

Fig. 3. Comparison of the enthalpy obtained from the Monte Carlo simulation data and the results estimated from the Peng–Robinson equation of state: ○, and ●, MC data for vapor and liquid phases, respectively; —, PR-EOS.

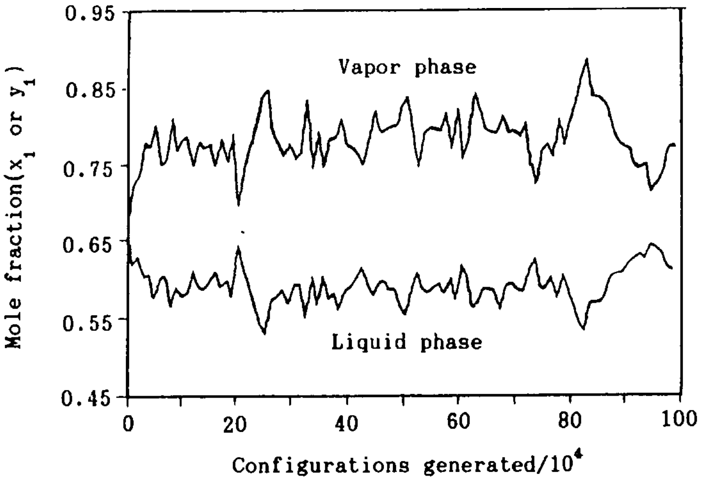

Fig. 4. Fluctuation chart of mole fractions for the Ar/CH_4 system at 150.72 K and 30.0 bar.

demonstrating the evolution of the simulation. We see that the simulated enthalpies are nearly the same as the estimation results of the EOSs. Because the cubic EOSs are generally considered to be reliable under thermodynamic conditions far removed from the critical point, the simulation data are also believed to be satisfactory.

DISCUSSION

In this work, we have simulated the enthalpies of the binary mixture argon (1) and methane (2) using the Gibbs-ensemble Monte Carlo simulation method. The simulation enthalpies are in good agreement with those calculated from the Peng–Robinson and Soave equations. The parameters used were obtained by applying the isothermal-isobaric ensemble to fit only the liquid density and the enthalpy of vaporization at the normal boiling point.

The components in the system investigated in this work are very simple. For complex compounds, we can separate the molecules, as in group contribution methods, into different groups. By fitting to the few structural and thermodynamic properties, we can tabulate the potential parameters for a variety of groups. With this table, we will be able to predict the phase equilibria of systems with little experimental data. Furthermore, more realistic models of potential functions should be adopted to produce more reliable data for industrial process designs.

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