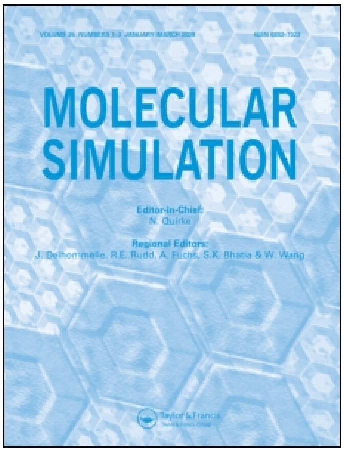

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T. Hauschild[a]; J. M. Prausnitz[a]
[a] Chemical Engineering Department and Chemical Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA

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MONTE-CARLO CALCULATIONS FOR METHANE AND ARGON OVER A WIDE RANGE OF DENSITY AND TEMPERATURE, INCLUDING THE TWO-PHASE VAPOR-LIQUID REGION

T. HAUSCHILD AND J.M. PRAUSNITZ

Chemical Engineering Department and Chemical Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

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The Gibbs-ensemble simulation technique provides a powerful method to calculate vapor-liquid phase behavior [1]. To evaluate the configurational energy of a system of molecules, commonly used experessions describe the interaction between two molecules. Contributions from higher-body forces are usually implicitly taken into account by adjusting two-body potential parameters to give agreement with experimental data. Explicit expressions for higher-body potentials are not commonly used in simulations [8]. The work by Smit *et al.* [9] gives the appropriate expressions to evaluate the pressure as well as the chemical potential from a density-dependent two-body potential in an NVT ensemble.

In the present work, contributions to the potential from two-body interactions are separated from those due to higher-body interactions; to take higher-body forces into account, a mean-field term, proportional to (density)$^{0.9}$, is added to the two-body potential. NPT-simulations over a wide range of temperature and density, as well as Gibbs-ensemble simulations, are used to evaluate phase behavior of argon and of methane. The results indicate that a simple mean-field correction to the "true" two-body Kihara potential provides good agreement between experiment and simulation.

KEY WORDS: Gibbs ensemble, density dependant potentials argon, methane.

1 INTRODUCTION

In the past decade, Monte-Carlo computer simulation has become accessible to predict thermophysical properties for some engineering purposes. Introduction of Gibbs-ensemble simulations has opened a wide field of application; the review by Panagiotopoulos [1] shows the potential success of this simulation method.

Many authors (e.g. [2] and [3]) have given attention toward applications of computer simulation. Only little attention has been given toward finding an efficient method to incorporate effects of higher-body interactions which contribute to the potential energy at moderate and high densities. A recent study by Luckas [4] concerning the thermophysical properties of fluid methane includes the effects of three-body forces through an Axilrod-Teller dispersion term, but this inclusion is cpu-time consuming and requires access to large main-frame computers. Although the Axilrod-Teller term for three-body intermolecular forces has little theoretical validity at small intermolecular distances [5], the results by Luckas [4] and those by Barker [16], [17] indicate that three-body forces make a major contribution to the internal energy at moderate and high densities. For liquid argon the portion of this contribution is estimated to be 10–15% [6].

De Pablo *et al.* [8] reported an attempt to combine the OPLS approach [7] using a site-site potential with the Gibbs ensemble; these authors found agreement between experimental data and calculations from Monte-Carlo simulations for selected binary hydrocarbon mixtures containing methane. The Lennard-Jones potential was chosen to represent the interactions between two sites and a set of effective site-site energy parameters was given; these parameters are density dependent. However, it was shown by Smit *et al.* [9], that these energy parameters are limited to the particular application shown, especially since they are restricted to the density and temperature range in which their density dependence had been adjusted.

In this work we focus on a less ambitious but more general semi-empirical method towards calculation of the fluid-phase diagram, including the two-phase region. In this method we include multibody contributions to the potential energy; except at low densities, we do *not* assume pair-wise additivity of intermolecular potentials.

2 MULTIBODY EFFECTS

We distinguish between two-body forces and higher-body forces. The components under investigation in this work are pure methane and pure argon. Both are considered as fluids containing single-site spherical molecules.

Evidence for two-body interactions between molecules is found in experimental second-virial-coefficient data. As discussed in numerous references, notably Hirschfelder [10], parameters for the Lennard-Jones potential can be fit to experimental second-virial-coefficient data; such a fit provides reasonable but not satisfactory agreement with the experimental results over a wide temperature range [11]. However, a similar fit to obtain parameters for the Kihara potential with a spherical hard core provides good agreement for methane and argon over a wide range of temperature. Table 1 presents Kihara parameters for methane and argon as given in ref. [11].

For systems of simple spherical molecules, the leading term for higher-body forces is a disperson contribution of a three-body Axilrod-Teller term [12] given by

$$u_{\text{Axilrod}} = \frac{\nu}{r_{ij} r_{ik} r_{jk}} (1 + 3\cos\theta_1 \, \cos\theta_2 \, \cos\theta_3) \qquad (1)$$

where ν is a characteristic constant, r is the intermolecular distance and θ is the angle defined by the vectors of distance between two pairs of molecules. The Axilrod-Teller term depends on intermolecular distance to the ninth power. The multibody potential energy correction term in this work u_{mb} is chosen such that it has an order of dimensions close to those in the Axilrod-Teller equation. The

Table 1 Kihara-potential parameters for methane and argon as given in Reference [11]; a is the radius of the hard core.

Component	*σ* *A*	*ε/k* *K*	*a* *A*	*Temperature range* *K*
Argon	3.317	146.52	0.179	85–873
Methane	3.565	227.13	0.393	125–623

correction term used here is a field term proportional to the 9/10 power of the overall density ($\rho^{0.9}$) as well as to the attractive-energy contribution from the two-body potential u_6. For the multibody (mb) contribution

$$u_{\mathrm{mb}} = \alpha\left(\frac{\rho}{\rho^{\mathrm{crit.}}}\right)^{0.9} u_6 \tag{2}$$

where ρ^{crit} is the density at the vapor-liquid critical point and

$$u_6 = -4\epsilon\left(\frac{\sigma-2a}{r-2a}\right)^6 \tag{3}$$

The expression for the potential energy considered here is given by

$$u = u_{\mathrm{Kihara}} - u_{\mathrm{mb}} \tag{4}$$

with the two-body Kihara potential given by

$$u_{\mathrm{Kihara}} = 4\epsilon\left[\left(\frac{\sigma-2a}{r-2a}\right)^{12} - \left(\frac{\sigma-2a}{r-2a}\right)^6\right], \quad r \geqslant 2a \tag{5}$$

$$u_{\mathrm{Kihara}} = \infty, \quad r < 2a \tag{6}$$

where ϵ is the minimum two-body potential energy, σ is the collision diameter and 2a is the diameter of the molecular hard core.

The adjustable constant α is found by comparison between prediction of liquid densities at a fixed temperature close to or at saturation and experimental data. Experimental data are taken from the compilation of Vargaftik [13] and from Sychev *et al.* [14].

Equation 4 obeys the necessary boundary condition that, as $\rho \rightarrow 0$, the two-body potential is recovered.

3 COMPUTATION

Monte-Carlo simulations were performed in an NPT ensemble to obtain predicted densities in the one-phase region. In addition, for methane, Gibbs-ensemble simulations provide predictions for the two-phase region of saturated liquid and saturated vapor at a given temperature.

All codes used in this work have been developed previously at Berkeley [15]. They were only slightly modified to include changes in the calculation of intermolecular energy. The Metropolis scheme is followed for statistical averaging.

The number of molecules for all NPT simulations was set equal to 256. The length of the simulated box with periodic bondary conditions was always larger than six times collision diameter σ. A spherical potential cut-off was taken at an intermolecular distance equivalent to approximately 45% of the box length. A volume move was attempted after 500 attempted particle moves. All runs were given a minimum of 10^6 steps for equilibration; an additional 10^6 steps were taken to obtain an average value for energy as well as for density. Gibbs-ensemble simulations were performed with a total of 350 molecules.

All calculations were performed on an IBM-3090 main-frame computer. For NPT simulations, about 3000 cpu seconds were required to perform 10^6 steps under conditions given above.

Table 2 Field-term parameter α

Component	α	*Adjusted at*
Methane	−0.001320	Saturated liquid density at 130 K
Methane	−0.000914	Saturated liquid density at 150 K
Argon	−0.003921 −0.0003136	Liquid density at 100 K Liquid density at 130 K

Table 3 Gibbs simulation of methane at various temperatures; experimental and predicted densities ρ of saturated vapor and saturated liquid; field-term parameter α and contribution C by multibody forces to the internal energy in the liquid phase.

T	α	ρ, *saturated vapor, g/cm*^{3}		ρ, *saturated liquid, g/cm*^{3}		*C*
K		*exp.*	*sim.*	*exp.*	*sim.*	*%*
130	−0.001320	0.00595	0.0120 ± 0.00056	0.3977	0.3895 ± 0.0116	15
150	−0.000914	0.0201	0.0223 ± 0.00035	0.3610	0.3656 ± 0.0122	10

Table 4 NPT simulation of methane at various temperatures and pressures; experimental and predicted ρ in the one-phase region; field-term parameter $\alpha = -0.001320$; contribution C by multibody forces to the internal energy.

T	*p*	ρ, *g/cm*^{3}		*C*
K	*MPa*	*Experimental*	*Simulated*	*%*
130	0.1	0.0015	0.0016 ± 0.00008	0
130	3.0	0.3998	0.3933 ± 0.0085	15.5
130	5.0	0.4021	0.4024 ± 0.0068	16
130	10.0	0.4075	0.4112 ± 0.0076	16
130	15.0	0.4124	0.418 ± 0.0073	16.5
130	30.0	0.425	0.4387 ± 0.0059	18
130	50.0	0.4386	0.4563 ± 0.0041	18.5
150	0.1	0.0013	0.00112 ± 0.0001	0
150	3.0	0.3654	0.3103 ± 0.0149	12
150	5.0	0.3693	0.3522 ± 0.0073	14
150	10.0	0.3778	0.3602 ± 0.0096	14
150	15.0	0.3851	0.3791 ± 0.0098	15
150	50.0	0.4188	0.4307 ± 0.0069	18
150	100.0	0.4466	0.4675 ± 0.0044	20
144.53	10.0	0.3846	0.3764 ± 0.0088	15
155	20.0	0.3846	0.3807 ± 0.0054	15
300	10.0	0.0751	0.0706 ± 0.0048	3
300	20.0	0.1549	0.144 ± 0.0082	6
300	50.0	0.2715	0.2643 ± 0.0065	11.5
300	100.0	0.3421	0.3407 ± 0.0074	15
500	20.0	0.0745	0.0746 ± 0.0054	3.5
500	50.0	0.161	0.1592 ± 0.0054	7.5
500	100.0	0.2446	0.2415 ± 0.0067	12
500	200.0	0.3283	0.3285 ± 0.0057	17

Table 5 NPT simulation of methane; field-term parameter $\alpha = -0.00914$ at $T = 150\,K$; simulation results without field term at $T = 130\,K$.

T *K*	*α*	*p* *MPa*	*Density, g/cm³* *Experimental*	 *Simulated*	*C* *%*
130	0.0000	5.0	0.4021	0.4987 ± 0.015	0
		15.0	0.4124	0.5057 ± 0.013	0
		30.0	0.425	0.5173 ± 0.009	0
150	−0.000914	10.0	0.3778	0.3940 ± 0.0109	10.5
		15.0	0.3851	0.4080 ± 0.0116	11
		50.0	0.4188	0.4512 ± 0.0058	12.5

Table 6 NPT simulation of argon at various temperatures and pressures; experimental and predicted densities ρ in the one-phase region; field-term parameter α; contribution C by multibody forces to the internal energy.

p *MPa*	*ρ, g/cm³* *Experimental*	 *Simulated*	*C* *%*	*ρ, g/cm³* *Simulated*	*C* *%*
		$\alpha = -0.0003921$		$\alpha = -0.0003136$	
T = 100 K					
0.1	0.0049	0.0048 ± 0.0001	0	0.0049 ± 0.0001	0
1.5	1.315	1.305 ± 0.019	11.5	1.341 ± 0.021	9
2.5	1.319	1.303 ± 0.018	11.5	1.339 ± 0.018	9
4.0	1.325	1.326 ± 0.020	11.5	1.351 ± 0.018	9
10.0	1.347	1.343 ± 0.016	12	1.386 ± 0.017	9.5
30.0	1.38	1.406 ± 0.011	12.5	1.438 ± 0.012	10
50.0	1.447	1.462 ± 0.011	13.5	1.486 ± 0.007	11
T = 130 K					
0.1	0.0037	0.0038 ± 0.00008	0	0.0041 ± 0.0001	0
4.0	1.090	1.009 ± 0.044	8.5	1.101 ± 0.034	7.5
5.0	1.102	0.994 ± 0.026	8.5	1.093 ± 0.033	7.5
10.0	1.147	1.091 ± 0.031	9.5	1.159 ± 0.025	8
15.0	1.182	1.159 ± 0.025	10	1.194 ± 0.014	8.5
30.0	1.255	1.238 ± 0.019	11	1.275 ± 0.020	9.5
T = 85 K					
2.5	1.414	1.425 ± 0.012	12.5	1.453 ± 0.010	10
T = 120 K					
2.5	1.170	1.116 ± 0.030	9.5	1.154 ± 0.037	8
4.0	1.182	1.139 ± 0.024	10	1.172 ± 0.027	8
T = 110 K					
2.5	1.25	1.204 ± 0.028	10.5	1.245 ± 0.023	8.5
T = 115.59 K					
10.0	1.25	1.21 ± 0.022	10.5	1.271 ± 0.025	9
T = 146.29 K					
50.0	1.25	1.233 ± 0.018	11.5	1.262 ± 0.017	9

4 RESULTS

The parameter α was adjusted to give agreement with experimental data at saturation for methane and close to saturation for argon, respectively. In Table 2 the parameter α is given as obtained from adjustment. Table 3 gives Gibbs-simulation results for methane. Tables 4, 5 and 6 give NPT-simulation results for methane and for argon, respectively. The power 9/10 of the density dependence was chosen to obtain better agreement with experimental data at high densities of methane.

Tables 4 and 6 as well as Figures 1 and 2 show satisfactory agreement between experimental data and simulation results over the entire range of density and temperature under investigation. At low densities, agreement is necessarily good due to the fit of the Kihara-potential parameters to second-virial-coeffecient data. At intermediate and high densities, the semi-empirical term in equation (4) corrects for the contribution of higher-body forces to the configurational energy. However, predictions of high liquid densities are less accurate at temperatures below the critical temperature. In addition, as shown by results for different field-term parameter α in Table 6, a temperature dependence of α must be included to find agreement with experimental data close to and at saturation.

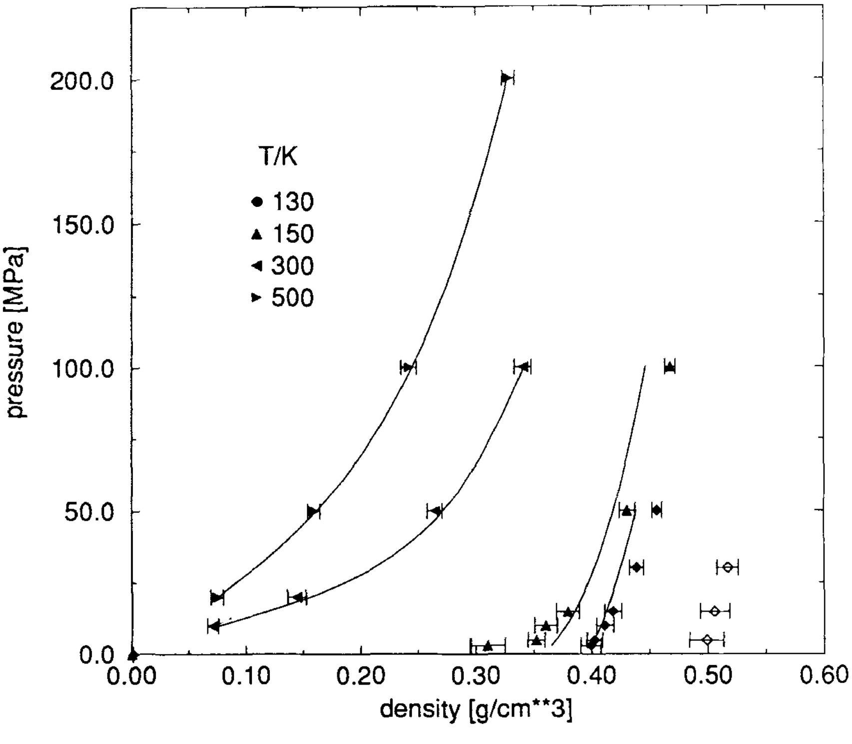

Figure 1 Pressure – density diagram for methane. Predicted results from simulation compared to experimental data over wide ranges of pressure and temperature; solid symbols are simulations results according to equation (4) and $\alpha = -0.001320$ while unfilled symbols are simulation results without field-term contribution to the potential energy.

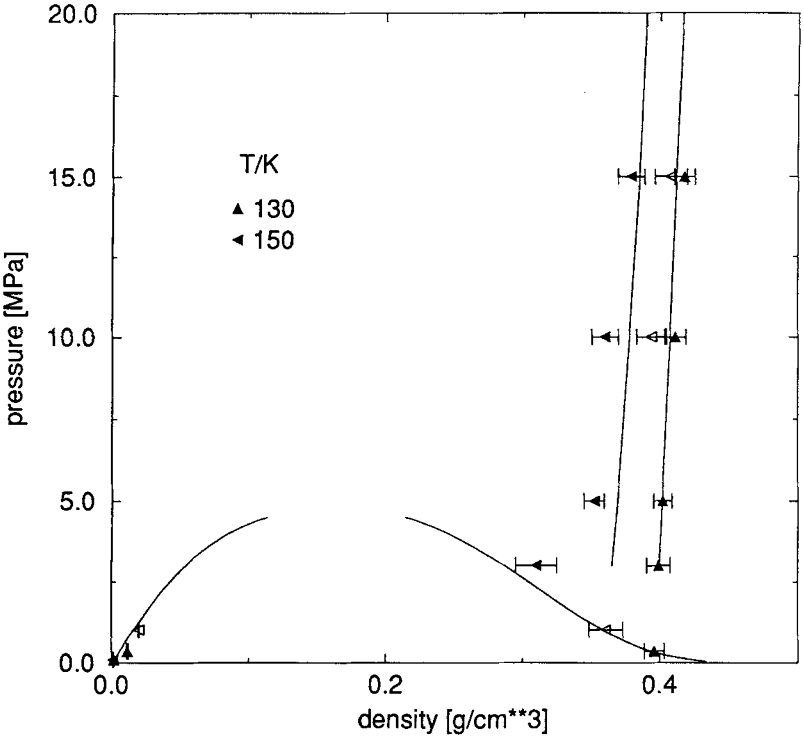

Figure 2 Pressure – density diagram for methane. Predicted results from simulation compared to experimental data close to saturation; solid symbols: $\alpha = -0.001320$, unfilled symbols: $\alpha = -0.000914$.

The contribution of higher-body forces is always positive and hence lowers the absolute value of the configurational energy. Table 5 gives simulation results without the field term in equation (4). The predicted densities differ approximately 20% from experimental values. Figure 3 shows that the multi-body contribution below the critical termperature of methane shows a linear behavior with density which is different from that at supercritical temperatures.

5 DISCUSSION

The semi-empirical potential function given in equation 4 appears to be reasonably successful for prediction of density over a wide range of temperature and pressure for argon and methane. Equation 4 extends cpu-time requirements only slightly when compared to simulations with density-independent effective-pair potentials. Pair-potential parameters (σ, ϵ, a) are available from second-virial-coefficient-data regression while parameter α, which corrects for multibody contributions to the internal energy, is obtained by adjustment at liquid-like densities close to or at saturation. The results indicate that α is temperature-dependent close to saturation.

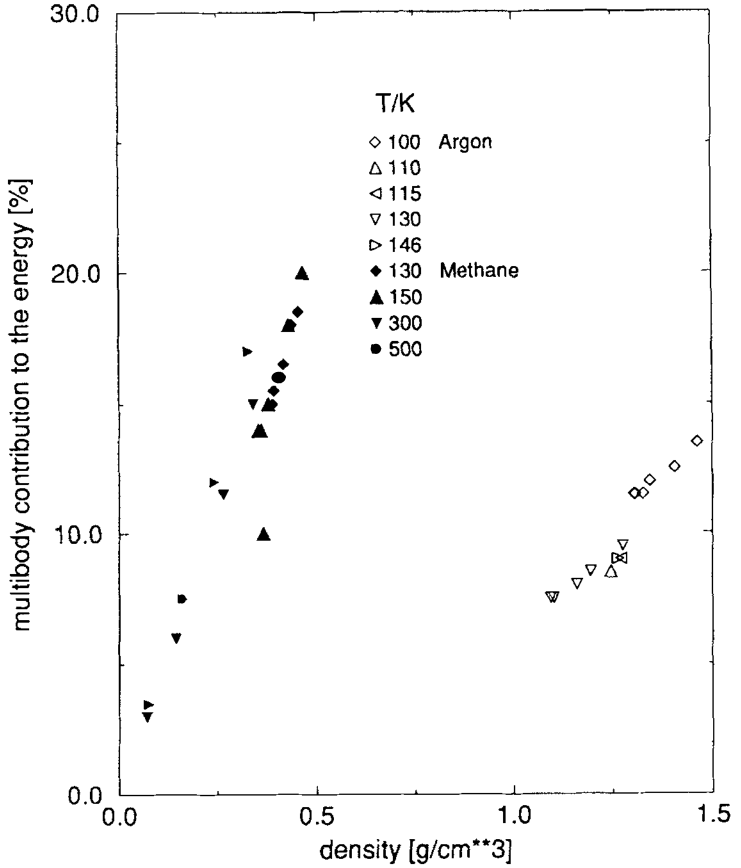

Figure 3 Multibody contribution to the internal energies of methane and argon at various temperatures; results according to Table 3, 4 and 6; results for argon at T = 100 K with $\alpha = -0.0.0003921$; all other results for argon with $\alpha = -0.0003136$.

Predicted densities are in good agreement with experimental. The accuracy is comparable to those of similar investigations in the literature reference [4], [18].

As found from simulation, the multi-body contribution to the energy is always positive in energy and contributes up to 20% (see Figure 1) at the highest density investigated for methane. For methane, the density dependence of the multibody-correction term u_{mb} at supercritical conditions is not the same as that at temperatures below critical.

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