Variational Perturbation Theory Compared with Computer Simulations[1]

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The variational perturbation theory has been applied to describe the compressibility of a 50% mixture of helium and nitrogen at room temperature and pressures up to 1 GPa. With parameters resulting from this perturbation theory, Monte Carlo simulations have been performed on model systems for these compounds as well as for the mixture. On comparison, clear restrictions are seen for the applicability of the perturbation theory combined with the one-fluid representation of mixtures.

KEY WORDS: mixtures; Monte Carlo simulations; variational perturbation theory.

1. INTRODUCTION

One of the ways of determining effective potential parameters is the application of the Ross variational perturbation theory [1]. In this theory the Helmholz free energy is written as the sum of an ideal repulsive part and a first-order correction term for the attractive part of the binary potential. For the latter, which is the potential energy of the system, the shape of the potential is chosen *a priori*. The value of the potential depends on the appropriate parameters that are found by a fit to experimental data. It has been proven that this approach works very well for the light gases He and Ne, if the Buckingham (the so-called exponential-6) potential is adopted. Parameter values have been found with which the experimentally determined density is well described up to very high pressures. This approach can also be applied to mixtures of gases, under the assumption that these

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mixtures can be represented by a one-fluid model. Given the Helmholz free energy F, the Gibbs free energy G follows from $G = F + pV$. An interesting feature is that the determination of the Gibbs energy as a function of the composition may reveal unstable states, and thus, a separation into two phases. The well-known bitangent method is used to determine the compositions of those phases. This method has been applied successfully to the He–H_2 system [2, 3]. Recently, accurate experimental data have become available for the density of He, N_2, and mixtures of these gases, in the pressure range of 0.1 to 1 GPa [4]. To obtain a high consistency all these data have been collected in the same experimental setup.

2. CALCULATIONS

To verify the applicability of the variational theory, Monte Carlo (MC) calculations have been performed on model systems for these compounds. First, we performed MC simulations for pure He and N_2, applying the binary exp-6 potential with parameters that have been published earlier [5]:

$$\varphi_{ij}(r) = \frac{6\varepsilon}{\alpha - 6} \left\{ e^{\alpha(1 - r/r_m)} - \alpha \left(\frac{r_m}{r} \right)^6 \right\}$$

For He: $\varepsilon/k = 9.76$ K; $r_m = 3.0826 \times 10^{-10} m$; $\alpha = 12.55$ (1)

For N_2: $\varepsilon/k = 85.0$ K; $r_m = 4.070 \times 10^{-10} m$; $\alpha = 14.55$

The fit was optimized at the very high pressures. Especially in the case of nitrogen a certain spread in values of the parameters was found. Second, simulations on the 50% mixture were performed in two ways: As a simulation of a real mixture, and as a simulation in which the system is represented by a one-component fluid. In the first case, parameters are needed for both pure components as well as for the unlike interactions, but in the second case, henceforth called the one-fluid model, only one set of parameters suffices. For the latter model, use has been made of the mixing rule as proposed by Ree [6], which relates the parameters for the representative one-fluid exp-6 potential to the pure-component parameters and the composition:

$$r_m^3 = (x_1^2 r_{m1}^3 + 2x_1 x_2 r_{m12}^3 + x_2^2 r_{m2}^3)$$

$$\varepsilon = (x_1^2 r_{m1}^3 \varepsilon_1 + 2x_1 x_2 r_{m12}^3 \varepsilon_{12} + x_2^2 r_{m2}^3 \varepsilon_2)/r_m^3$$ (2)

$$\alpha = (x_1^2 r_{m1}^3 \varepsilon_1 \alpha_1 + 2x_1 x_2 r_{m12}^3 \varepsilon_{12} \alpha_{12} + x_2^2 r_{m2}^3 \alpha_2)/(\varepsilon r_m^3)$$
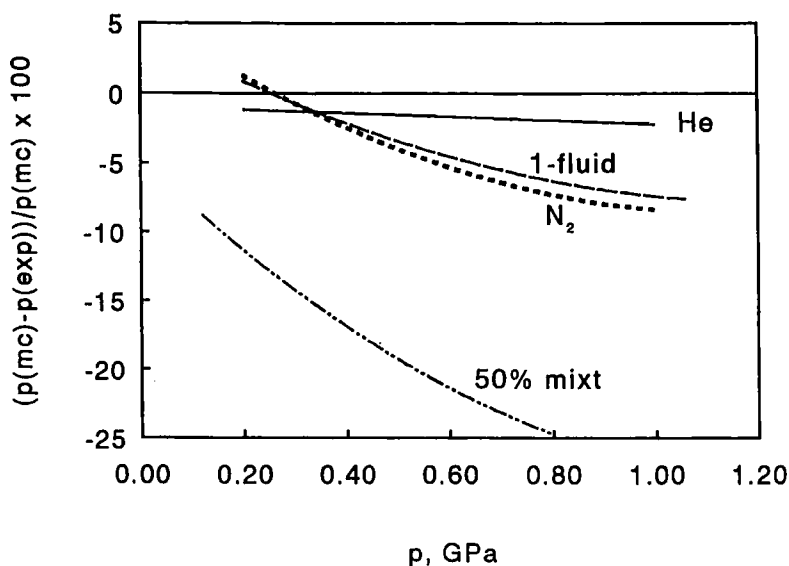
Fig. 1. Relative deviations of the pressure, obtained by Monte Carlo simulations, versus the experimental data at 298.15 K.

subscript i denotes component i; ij denotes the unlike interactions. Inserting the pure component parameters and adjusting both the one-fluid parameters and the unlike-interaction parameters in such a way that an optimal agreement between the variational method and the experimental data is obtained, results in the following values. For the one-fluid model

$$\varepsilon/k = 39.95 \text{ K}; \qquad r_m = 3.61 \times 10^{-10} m; \qquad \alpha = 14.27$$

for the unlike interaction between He and N_2 molecules (3)

$$\varepsilon/k = 16.50 \text{ K}; \qquad r_m = 3.58 \times 10^{-10} m; \qquad \alpha = 13.55$$

The results of the simulations for pure He, pure N_2, the 50% mixture according the one-fluid model and the real mixture model are given graphically in Fig. 1, which displays the relative deviations of the calculated values from the experimental data. Each series of calculations consists of nine points; the standard deviations were always less than 0.5%. For simplicity, only smooth curves are presented. The following conclusions are obvious:

    (1)   the simulation results for He deviate no more than 2% from the experimental data;

    (2)   the simulation results for N_2 deviate 5% or more;

(3) the deviations for the one-fluid simulation are of the same quality as the N_2 simulation results; and

(4) the simulations on the real 50% mixture, using the unlike inter-action that resulted from the perturbation theory and the one-fluid approach as given in 3 reveal a large discrepancy with the experiments, of up to 25%.

The last two observations imply an inconsistency because the unlike parameters and the one-fluid parameters are determined simultaneously. Possible reasons for inconsistency are: The one-fluid model is not realistic, the perturbation theory is not applicable, the exp-6 potential may not be realistic for any of the interactions, or the parameters used are substantially wrong.

Even more serious objections against the one-fluid and the perturbation theory arise when the Gibbs energy of the mixture, represented by the one-fluid model is calculated. With the parameters mentioned, a phase separation is predicted just above 1 GPa, while experiment shows that the separation starts above 7 GPa [7]. It is conceivable that the one-fluid theory will give wrong results in the case that the difference between intermolecular potentials of the components exceeds certain limits. Usually it is assumed that the ratio of the well depths is less relevant for the applicability of this theory but that the model is not valid for ratios of the diameter above about 1.3, namely, slightly more than in our model system.

In this study, we demonstrate the influence of the choice of the unlike parameters in the following way. MC calculations have been performed on mixtures of the N_2 model with 50% of an imaginary fluid X; all at a molar density of 38.884 kmol $\cdot$ m^{-3} and a temperature of 298.15 K. The results of the calculations for the pressure and energy are given in Table I including the statistical uncertainties ($+/-$). First, the potential for X was chosen in conformity with that of He: Model $X0$. It is evident that the one-fluid result is much too high, in comparison with the 50% mixture model (332 vs 289 MPa). Next the same diameter as for N_2 was taken, model $X1$: Again, a too high result for the pressure is seen. Model $X2$ has the same well depth as N_2, but the diameter of He; now the results are approximately the same. For model $X3$ which only differs in α with N_2 the mixing rule for α is justified. Finally, the results for model $X4$, $X5$, and $X6$, all with the same diameter r_m but with increasing well depth, show that real mixtures and the corresponding one-fluid models are not consistent if the ratio of the well depths exceeds the value 3. This is a remarkable result, because it is generally assumed that a large difference in diameter is the most important limitation of the one-fluid approach [8].

Table I. MC Results for the Pressure and Energy of Nitrogen, Fictive Fluids, and 80% Mixture at 38.884 $kmol \cdot m^{-3}$

Components	Parameters			MC results			
	α	ε/k	r_m	p (MPa)	$\pm$	U_i/RT	$\pm$
$X0$	12.550	9.76	3.0826				
N_2	14.550	85.00	4.0700	949	6	−0.495	0.012
50% $X0$–N_2	13.550	16.50	3.5800	289	1	−0.193	0.004
1-f. $X0$–N_2	14.273	39.95	3.6120	332	1		
$X1$	14.550	9.76	4.0700	424	2	0.591	0.006
50% $X1$–N_2	14.550	16.50	4.0700	547	4	0.250	0.016
1-f. $X1$–N_2	14.550	31.94	4.0700	652	4	0.432	0.004
$X2$	14.550	85.00	3.0826				
50% $X2$–N_2	14.550	85.00	3.5800	363	3	−0.910	0.006
1-f. $X2$–N_2	14.550	85.00	3.6119	352	3		
$X3$	12.550	85.00	4.0700	735	4	−0.716	0.013
50% $X3$–N_2	13.550	85.00	4.0700	840	4	−0.604	0.016
1-f. $X3$–N_2	13.550	85.00	4.0700	840	5	−0.606	0.014
$X4$	12.550	9.44	3.1308				
50% $X4$–N_2	13.550	28.33	3.6004	315	2	−0.257	0.004
1-f. $X4$–N_2	14.178	45.26	3.6308	341	2	−0.239	0.005
$X5$	12.550	18.89	3.1308				
50% $X5$–N_2	13.550	40.07	3.6004	332	2	−0.364	0.004
1-f. $X5$–N_2	14.063	52.50	3.6308	346	2	−0.356	0.004
$X6$	12.550	28.33	3.1308				
50% $X6$–N_2	13.550	49.07	3.6004	342	2	−0.457	0.004
1-f. $X6$–N_2	13.985	58.40	3.6308	346	2	−0.462	0.004

The applicability of the variational perturbation theory is restricted to spherically symmetric potentials. In this study the exp-6 model was chosen for all interactions. For nitrogen, this may not be an optimal model. Nevertheless, it was considered useful to look for an optimal set of parameters for which the pressure of this model system, obtained with MC simulations, corresponds with experimental data. By trial and error, the following set was found for N_2 at 298.15 K, in the pressure range from 0.1 to 1.0 GPa:

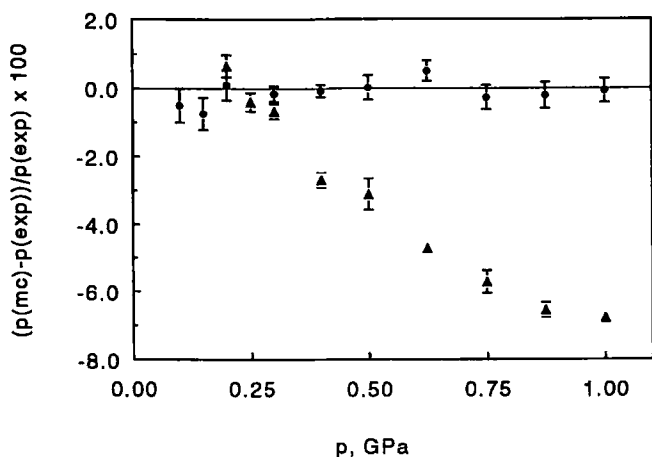$$\varepsilon/k = 100 \text{ K}; \qquad r_m = 4.075 \times 10^{-10} m; \qquad \alpha = 14.55 \qquad (4)$$

Fig. 2. Relative deviations of the pressure, obtained by Monte Carlo simulations, for nitrogen at 298.15 K. (▲) $\varepsilon/k = 85$ K; $r_m = 4.070 \times 10^{-10} m$; $\alpha = 14.55$; (●) $\varepsilon/k = 100$ K; $r_m = 4.075 \times 10^{-10} m$; $\alpha = 14.55$.

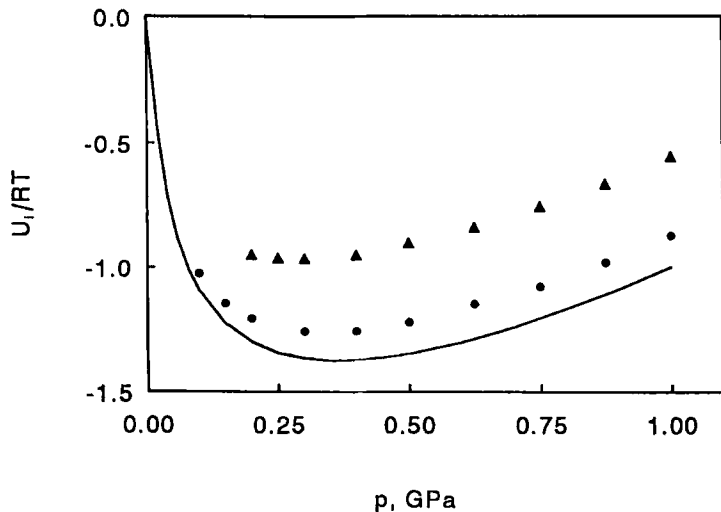**Fig. 3.** Internal energy of nitrogen at 298.15 K as a function of pressure. Monte Carlo results: (▲) $\varepsilon/k = 85$ K; $r_m = 4.070 \times 10^{-10} m$; $\alpha = 14.55$; (●) $\varepsilon/k = 100$ K; $r_m = 4.075 \times 10^{-10} m$; $\alpha = 14.55$; full curve, experimental [6].

The results are given in Fig. 2, together with the results based on previously mentioned parameters (1), obtained with the perturbation theory [4].

It is interesting to compare also the internal energy, calculated in the simulations via $U_i = \langle 1/N \sum \varphi_{ij} \rangle$ [φ_{ij} defined in (1)], for both parameter sets and with the experimental values. The latter have been obtained from the IUPAC tables [9], and the relation $U_i = H - pV + U_0$, where H denotes the enthalpy, and $U_0 = \lim(V \to \infty) U_i$. Figure 3 demonstrates a clear improvement with the new parameters (4), although a systematic deviation remains. Similarly, new parameters for He have been found that give a slightly better correspondence for the pressure–density relation in the pressure range up to 1 GPa:

$$r_m = 3.09 \times 10^{-10} m; \qquad \varepsilon/k = 9.60 \text{ K}; \qquad \alpha = 12.55 \qquad (5)$$

No experimental values for the internal energy of helium up to 1 GPa are available. Monte Carlo simulations offer the possibility to appoint a parameter set for the unlike interactions. For this purpose simulations on a 50% mixture have been performed, with the new parameters for He and N_2 and with unlike interaction parameters obtained by trial and error. The unlike interaction parameters have been chosen in such a way that the experimental density was reproduced by the simulations at three distinct pressures, namely, at 0.18, 0.47, and 0.95 GPa. It was assumed that the value of 13.55 for α, which is the average of the He and N_2 values, was acceptable. A series of calculations at each pressure gave a relation between ε/k and r_m. In Fig. 4 these relations are displayed as full curves. At the crossing of these curves, the optimum values of the unlike-interaction parameters are found:

$$r_m = 3.73 \times 10^{-10} m; \qquad \varepsilon/k = 22.5 \text{ K} \qquad (6)$$

For comparison, the Lorentz–Berthelot parameters for unlike-interaction, defined as

$$r_m = \frac{r_{m_1} + r_{m_2}}{2}$$

$$\varepsilon = (\varepsilon_1 \cdot \varepsilon_2)^{1/2} \qquad (7)$$

$$\alpha = (\alpha_1 \cdot \alpha_2)^{1/2}$$

are also indicated in the figure, revealing a large discrepancy. The same procedure has been applied for the determination of one-fluid parameters. The result is given in Fig. 5; parameter values are

$$r_m = 3.595 \times 10^{-10} m; \qquad \varepsilon/k = 50.5 \text{ K} \qquad (8)$$
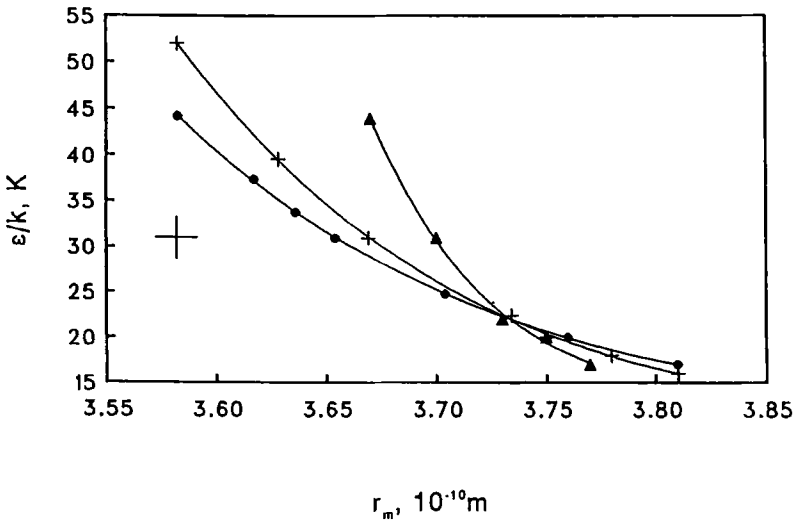
Fig. 4. Monte Carlo results for the relation between well depth and potential radius for the unlike interaction in a helium–nitrogen mixture, at constant pressure and density. Triangles, 0.18 GPa; crosses, 0.47 GPa; circles, 0.95 GPa. For other parameters, see text. The cross indicates the values from the Lorentz–Berthelot rule.
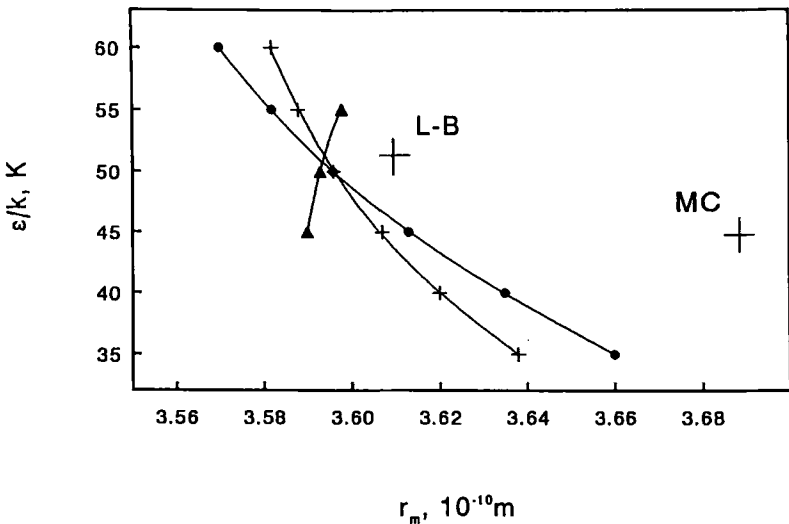

Fig. 5. Monte Carlo results for the relation between well depth and potential radius for the one-fluid model of a 50% helium–nitrogen mixture, at constant pressure and density. Triangles, 0.18 GPa; crosses, 0.47 GPa; circles, 0.95 GPa LB: Lorentz–Berthelot parameters in Eq. (2). MC: Unlike interaction parameters from Monte Carlo simulation in Eq. (2).

Substitution of the new parameters for He and N_2 given in (4) respectively (5) in the Lorentz–Berthelot rule results in values also given ("LB"). Substitution of these parameters for He, N_2, and the new unlike parameters (6) in the combining rule Eq. (2) results in the values indicated with "MC." Especially the difference of the one-fluid paraeters (8) and the MC ones is dramatic: The 50% one-fluid model leads to much too high results at all conditions considered. With the new parameters Eqs. (4)–(6) simulations have been performed for systems with 0 to 100% N_2 (increasing in steps of 10%) at 39 kmol $\cdot$ m^{-3} at 300 K. Next, for the same conditions, the one-fluid system with parameters obtained by substitution of Eqs. (4)–(6) in Eq. (2) has been considered. We found that the one-fluid results for the pressure are always too high; by roughly 10–15% for mixtures with less than 80% N_2, by 5% at 80% N_2, and by 2% at 90% N_2. It must be emphasized that this inconsistency is independent of the question whether or not the real systems are well presented by the adopted potential: The one-fluid model leads, in all circumstances, considered to an overestimation of the pressure.

3. CONCLUSION

We have demonstrated that the perturbation theory, combined with the one-fluid approach, may lead to considerable inconsistencies for mixtures of components with large differences in potential strength. This is not due to the approximations of the potentials, such as additivity and idealized analytic presentation of the potential function. The one-fluid theory is not valid if the ratio of the well depths is larger than three.

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