TOWARDS AN EFFECTIVE INTERMOLECULAR POTENTIAL ENERGY FUNCTION FOR FLUID TETRAFLUOROMETHANE

JORGE C. G. CALADO (1)
Complexo I, Instituto Superior Técnico, 1096 Lisboa, Portugal

PAULETTE CLANCY
School of Chemical Engineering, 254 Olin Hall, Cornell University, Ithaca, N.Y. 14853, USA

(Received 19 August 1985)

ABSTRACT — The development of an intermolecular potential energy function for carbon tetrafluoride is outlined, which is able, when used in conjunction with a perturbation theory, to accurately predict a variety of PVT properties over wide ranges of temperature and pressure (120-400 K, 0-110 MPa). The importance of anisotropic forces in the dense fluid region for this molecule is clearly demonstrated, the most significant forces arising from the non-spherical shape of the molecule rather than its multipolar interactions.

1 – INTRODUCTION

The ability to predict P - V - T data over wide ranges of density and temperature is, perhaps, one of the strictest tests of intermolecular potentials. It is well-known [1] that second-virial coefficients do not generate a unique potential and recent potential-inversion techniques [2] for this property and transport properties can only generate gaseous potentials for spherical or quasi-spherical molecules. Transport properties, which are another source of potential functions, are difficult to measure accurately.

In perturbational and variational treatments, intermolecular potentials are usually developed by requiring agreement with experimental data along the saturation line (usually vapour pressures and liquid densities) often because accurate P - V - T data

---

(1) Author to whom correspondence should be addressed.

over extended pressure and temperature ranges are not available. However, as we have recently shown for ethylene [1], orthobaric data may not define the intermolecular potential in a unique way. That definition can only be reliably achieved by testing the potential against the whole phase surface of the substance. This supports the claim of Powles *et al.* [3] that there is an urgent need for configurational energy data over wide ranges of density and temperature, in order to properly test theories and improve intermolecular potential functions.

We have recently completed such a study for tetrafluoromethane, CF_4 [4]. Thirty-three isotherms, covering the temperature range 95-413 K and pressures up to 110 MPa have been studied, resulting in over one thousand and five hundred data points. This amount of data should enable us to develop an effective and flexible intermolecular potential energy function for CF_4, which can then be applied to predict properties of systems of which CF_4 is a component.

Despite its apparent simplicity, tetrafluoromethane is an attractive substance from both the industrial and theoretical points of view. It has a low order of toxicity and a remarkable thermal stability. As Freon-14, it is widely used as a low-temperature refrigerator and sometimes as a gaseous insulator. On the other hand, CF_4 molecules display an interesting degree of anisotropy, as manifested in the intermolecular potential function, which any successful theory must be able to account. Whilst the gross features of the CF_4 molecules may be considered to be representable by a quasi-spherical or globular model, the thermodynamic behaviour of the substance, especially in mixtures, displays a non-ideality which is characteristic of the anisotropy present at the molecular level [5]. Even the existing low-density studies lead to contradictory conclusions about the intermolecular potential of CF_4. While some authors claim that a simple (12,6) Lennard-Jones potential

$$u(r) = 4\varepsilon\,[(r/\sigma)^{12} - (r/\sigma)^{6}] \qquad (1)$$

is able to describe the second virial coefficient data [6], others have argued that a spherical-shell model is necessary [7]. Tetrafluoromethane is then an intermediate case between those of methane, CH_4 (which can roughly be treated as spherical) and of tetrachloromethane, CCl_4 (which displays strong anisotropy and requires a spherical-shell or site-site model). The discriminating factor would appear to be the octopole moment (the first non-zero electric moment exhibited by a tetrahedral molecule) which is a measure of the electronic non-centrality of the molecule.

Strong orientational correlations, which seem to persist over several molecular diameters, have been found for tetrahedral molecules [8]. Interlocking effects have also been detected in CCl_4 molecules, using Brillouin scattering techniques [9]. In addition, calculations carried out using the site-site distribution function formulation show that the disagreement with results from computer simulation is much larger than for diatomic molecules [10]. All these facts seem to add up to the general conclusion that despite their apparent simplicity (small size, higher symmetry, non-polarity) CF_4 molecules offer enough problems to make a systematic study of its underlying potential worthwhile.

2 — THEORY AND PROPOSED MODELS

A spherical reference based perturbation theory approach due to Gubbins, Gray and co-workers [11-13] was used to evaluate the Helmholtz energy and hence all other thermodynamic properties of CF_4 from a knowledge of the dominant isotropic and anisotropic contributions to the intermolecular potential energy function, by the use of Statistical Mechanics techniques. The intermolecular pair potential $u(\mathbf{r}\,\omega_1\,\omega_2)$ depends on the molecular orientations $\omega_i\,(=\theta_i\,\phi_i\,\chi_i$ for non-linear molecules$)$ as well as the intermolecular separation, r. Such a potential may be separated into isotropic and anisotropic parts

$$u(\mathbf{r}\,\omega_1\,\omega_2) = u_0(r) + u_a(\mathbf{r}\,\omega_1\,\omega_2) \qquad (2)$$

where u_0 is a reference pair potential of isotropic particles and u_a contains all the orientation-dependent terms. The reference potential is given by

$$u_0(r) = \langle u(\mathbf{r}\,\omega_1\,\omega_2)\rangle_{\omega_1\,\omega_2} \qquad (3)$$

where $\langle \ldots \rangle$ denotes an unweighted average over orientations ω_i.

The Helmholtz energy, A, may be expanded in powers of the perturbing potential as

$$A_{\text{total}} = A_0 + A_1 + A_2 + A_3 + \ldots \qquad (4)$$

With the choice of a reference potential given by Eq. (3), the first order term, A_1, vanishes. The series expansion is slowly convergent, but for moderately polar molecules its sum can be obtained from a Padé approximant

$$A_{\text{total}} = A_0 + A_2 \; (1 - A_3 / A_2)^{-1} \qquad (5)$$

where A_i is the ith order term in the series. Detailed expressions relating A_i to the underlying intermolecular forces have been given previously (see, for example, ref. [11]) and will not be repeated here.

The major thrust of this paper lies in the development of the best possible effective intermolecular potential energy function for CF_4 which is able to give the closest prediction of experimentally determined thermodynamic properties over as wide a range of state conditions as possible, thus providing the most stringent test of the flexibility and dependability of the model potential. For CF_4, it will be interesting to try to ascertain whether a spherical, isotropic model for this molecule is indeed sufficient to reproduce the thermophysical properties of the fluid as has been suggested by some authors [6], to determine whether anisotropic forces contribute significantly to these properties and, if so, which anisotropic forces are the most important. Several candidates for orientation-dependent forces suggest themselves for this fluid. CF_4 is known to have a reasonably large octopole moment ($\Omega_{CF_4} = 4.8 \times 10^{-34}$ esu) and we might expect the spatial anisotropy of the molecule's electronic structure to cause charge overlap forces to be significant. In order to test the relative contributions of these terms we proposed four models, building on the isotropic potential model (which constitutes model A) in a stepwise fashion, thus:

Model A: $u = u_0^{(n,6)}$

Model B: $u = u_0^{(n,6)} + u_{\Omega\Omega}$ (336)

Model C: $u = u_0^{(n,6)} + u_{\Omega\Omega}$ (336) $+ u_{\text{dis}}$ (303 + 033)

Model D: $u = u_0^{(n,6)} + u_{\Omega\Omega}$ (336) $+ u_{\text{dis}}$ (303 + 033) $+ u_{\text{ov}}$ (303 + 033) where: u is the intermolecular potential energy; $u_0^{(n,6)}$ is the contribution from the reference fluid, here a Lennard-Jones (n, 6) potential; $u_{\Omega\Omega}$ is the anisotropic octopole-octopole interaction; u_{dis} is that due to the anisotropic dispersion; and u_{ov} is that arising from anisotropic charge overlap forces. The figures in brackets refer to the leading term or terms in the spherical harmonic expansion of these interactions. Such a method of determining the quality of the proposed model was used recently for ethylene [1], with considerable success.

The thermodynamic properties of the reference fluid were obtained using a methane equation of state [14]. This has been shown previously [5] to provide a better reference system for CF_4 than the more commonly employed argon reference used, for example, in most of the proposed models for ethylene in reference [1]. The potential model for CF_4 used in reference [5] is that given as model D here, and we shall use exactly that potential (with accompanying potential parameters) as our model D to test its efficacy in predicting PVT and other thermophysical properties.

The adjustable potential parameters involved in each of the models (the Lennard-Jones parameters ε / k, σ and n for models A - D and the shape parameter δ_3 appearing in u_{ov} in model D) were obtained by fitting to the experimental saturation line values for ρ_{liq} and P_{liq} [15]. Experimental values for the octopole moment (Ω) and dispersion coefficient (β_7) were employed in each model where appropriate. For CF_4 it was found to be considerably more difficult than usual to determine an acceptably invariant set of parameters over the whole saturation curve. It was possible to obtain a similar quality of fit to the coexistence properties with each of the models tested, underlining once again that these properties do not provide a route to a unique potential model for any fluid. The potential parameters determined in this manner for each of the models are given in Table 1. Using these models, the PVT properties from 120-400 K and from 0-110 MPa were predicted with no further adjustment of parameters.

3 – RESULTS

Several key PVT properties were predicted using each of the potential models described in the preceding section, over as wide a range of temperature and pressure as the theory (and the reference equation of state) would allow. The resulting theoretically predicted values were compared with recent, extensive experimental data due to Rubio *et al.* [4]. Isotherms from 120-400 K and pressures from 0-110 MPa were investigated, excluding state points where the reduced density, $\rho\sigma^3$, exceeds 1.05 (the limit of the methane equation of state), and temperatures close to the critical region (210-240 K), where the theory is invalid.

TABLE 1 — Potential Parameters for CF_4 Models

Model	n	$(\varepsilon/k)/K$	σ/A	$\Omega \times 10^{34}$/esu	β_7	δ_3
A	20	232.7	4.255	—	—	—
B	18	221.2	4.260	4.8	—	—
C	20	231.7	4.230	4.8	-0.20	—
D	20	232.0	4.250	4.8	-0.20	0.10

TABLE 2 — Average Percentage Deviation Between Theory and Experiment (120-210 K, 0-110 MPa)

Model	$\lvert\Delta\rho\rvert$ %	$\lvert\Delta U^c\rvert$ %	$\lvert\Delta S^c\rvert$ %
A	1.54	4.09	5.42
B	1.63	4.65	5.40
C	1.22	5.29	6.90
D	0.58	5.03	8.20

The most important property in this study is that of the density, due to its sensitivity to the intermolecular potential and its key value in industrial applications. Its prediction by each of the models is summarized in Table 2, where the average deviation between theory and experiment is given covering the whole temperature and pressure ranges. This information is disseminated in Figure 1 to show the deviation between theory and experiment as a function of (sub-critical) temperature. It can be seen that the full anisotropic potential (model D) is clearly superior to that of a simple Lennard-Jones model (model A). It is interesting to note

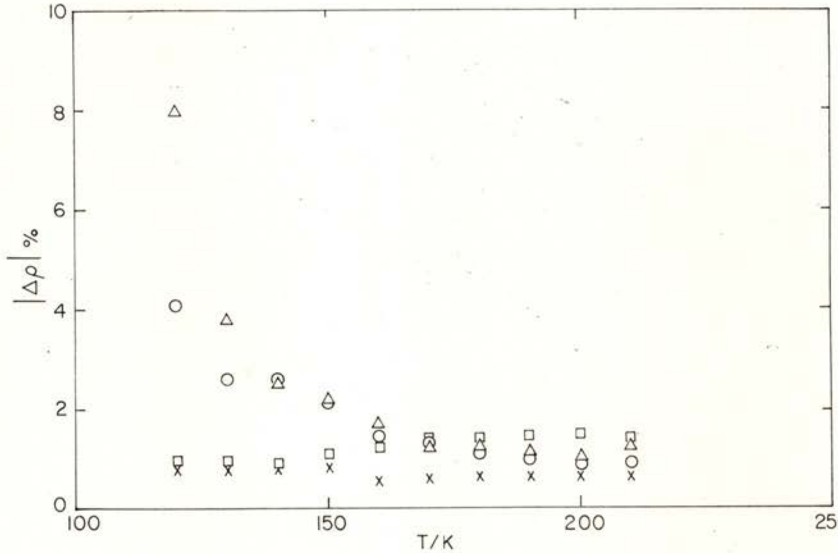

Fig. 1 — Deviation between theory and experiment for the density of CF_4 as a function of temperature: ○, model A; △, model B; □, model C; x, model D.

from this figure that the major improvement in predicting the density arises not from the addition of the octopolar forces (compare the results of models A and B), but from the addition of the shape forces (compare models C and D). The prediction of the density (and the other PVT properties) at supercritical temperatures is of much less interest. At high temperatures the effect of the anisotropy is 'washed out' by the higher kinetic energy of the molecules and any useful distinction between the potential models is precluded. The performance of the full anisotropic potential (model D) in predicting the density of CF_4

over wide density and temperature ranges can be fully appreciated in Figure 2, where the experimental results are compared with those from perturbation theory. Table 3 lists both the experimental and calculated values of density at round values of temperature and pressure.

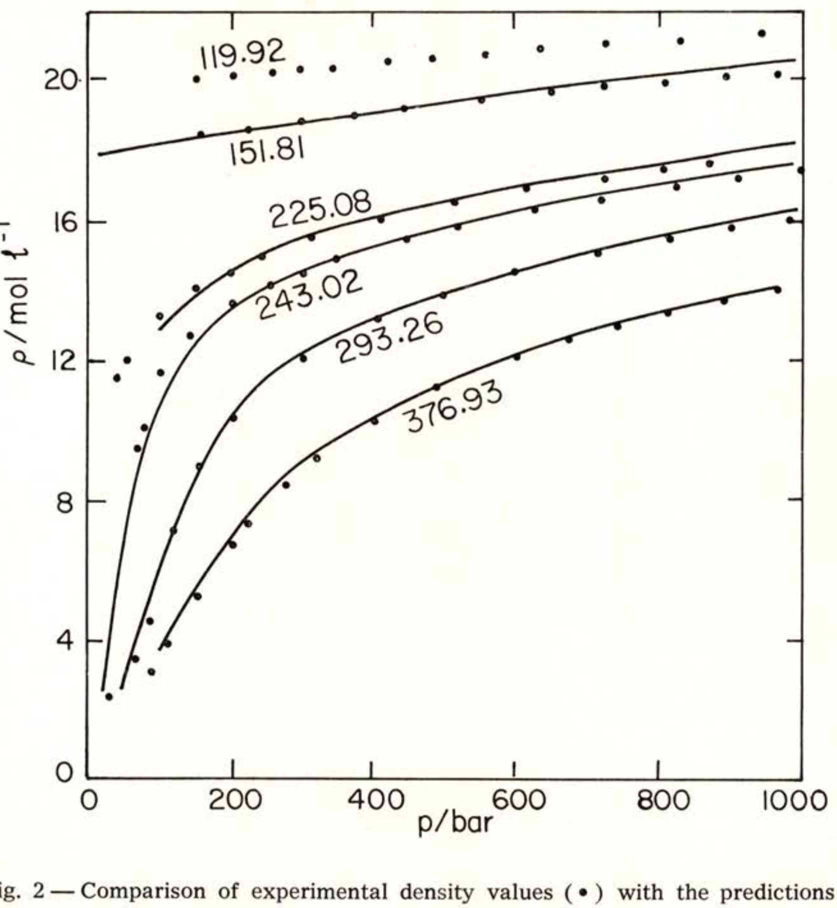

Fig. 2 — Comparison of experimental density values (•) with the predictions of perturbation theory using potential model D (—), as a function of pressure, for several isotherms.

The prediction of the configurational internal energy, U^c, was also investigated; results for this are shown in Table 2 and

TABLE 3 — Comparison of Experimental Values and Theoretical Prediction of the Density of CF_4 from 120-200 K and 25-1100 bars

T/K	120		140		160		180		200	
P/bar	Expt.	Theory *	Expt.	Theory *	Expt.	Theory *	Expt.	Theory *	Expt.	Theory *
25	19.790	19.760	18.659	18.553	17.438	17.448	16.058	16.116	14.332	14.073
50	19.852	19.824	18.745	18.635	17.565	17.566	16.260	16.311	14.716	14.641
100	19.970	19.950	18.908	18.795	17.796	17.787	16.606	16.646	15.287	15.297
200	20.188	20.218	19.198	19.095	18.190	18.180	17.152	17.185	16.069	16.111
300	20.385	20.434	19.454	19.376	18.521	18.526	17.583	17.626	16.632	16.687
400	20.567	20.895	19.684	19.642	18.810	18.838	17.943	18.005	17.081	17.151
500	20.735	21.086	19.893	19.898	19.067	19.123	18.256	18.340	17.458	17.548
600	20.892	21.609	20.085	20.152	19.299	19.387	18.533	18.642	17.785	17.897
700	21.039	—	20.264	20.266	19.512	19.634	18.783	18.918	18.074	18.209
800	21.179	—	20.431	20.469	19.709	19.867	19.011	19.173	18.336	18.495
900	21.311	—	20.588	20.943	19.892	20.088	19.221	19.411	18.574	18.757
1000	21.437	—	20.736	21.185	20.063	20.305	19.417	19.633	18.793	19.000
1100	21.557	—	20.877	21.297	20.225	20.518	19.599	19.844	18.997	19.228

* Theory results correspond to potential Model D.

Figures 3 and 4. This property is of somewhat less importance than the density, its experimental value being derived rather than

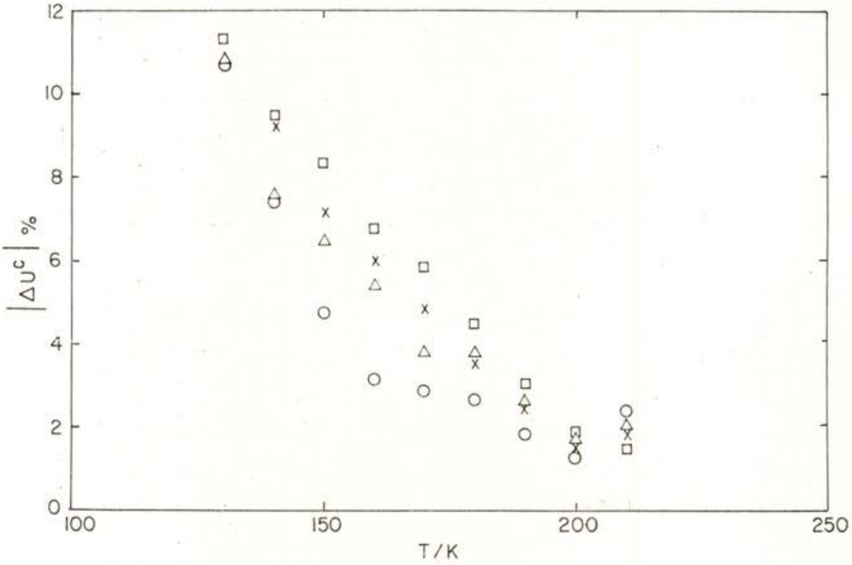

Fig. 3 — Deviation between theory and experiment for the configurational energy U^c of CF_4, as a function of temperature: ○, model A; △, model B; □, model C; x, model D.

fundamental and subject to more uncertainty (~5 %). The theoretically predicted values do not have the accuracy obtained for the density but give an adequately good description of the experimental values. Here, unlike for the density, no clear improvement is produced by adding anisotropic forces to the potential. The overall prediction of the internal energy for model D is numerically not quite as good as that of model A, but the difference is not particularly significant given the experimental uncertainly.

The results for the configurational entropy S^c in terms of the observed trends between models mirror those for U^c, although the prediction of this property is significantly poorer for all the models studied as can be seen in Table 2.

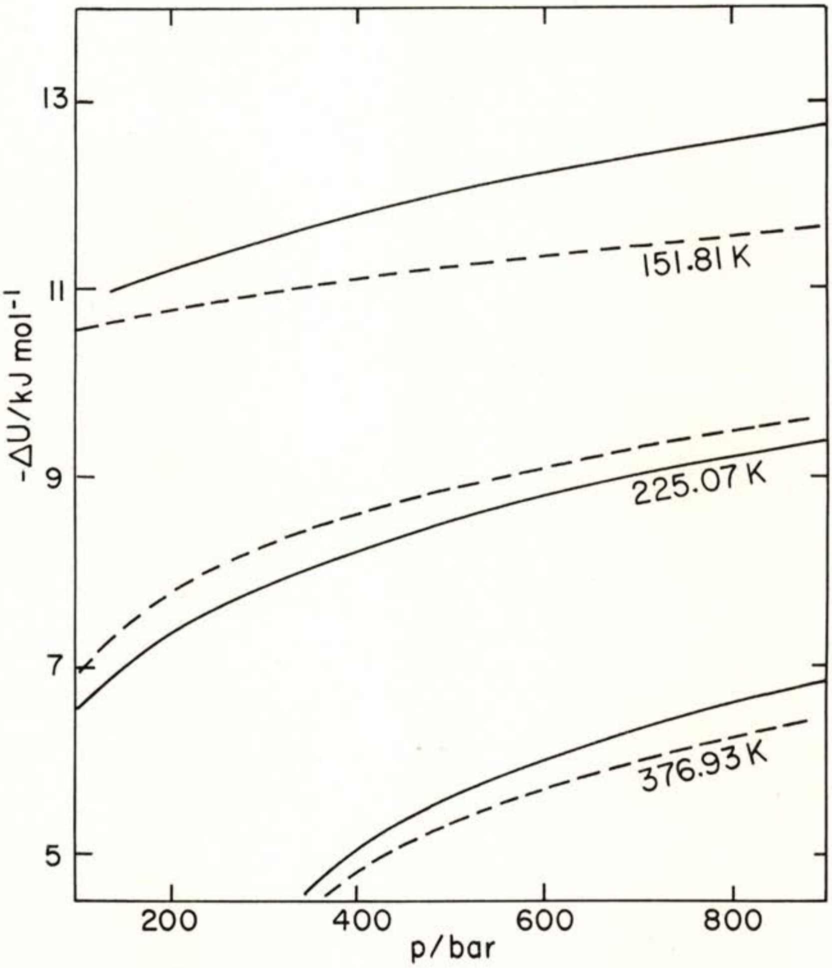

Fig. 4 — Comparison of "experimental" configurational energy, derived from the experimental values of density (——), and the predicted one by perturbation theory (— —), using potential model D.

4 – DISCUSSION

The development of an effective fluid potential for carbon tetrafluoride using a perturbation theory approach is clearly a difficult task; indeed it has been suggested [16] that this molecule is probably too far from sphericity to be adequately represented by such a procedure. It has already been noted that the determination of the potential parameters is particularly difficult for this fluid. Fortuitously, however, the prediction of the PVT properties appears to be relatively unaffected by this choice. The prediction of the most discerning property, the density, shows a clear distinction between the proposed models, with the importance of including the anisotropy of the molecule clearly demonstrated over a purely isotropic Lennard-Jones model. It was interesting and somewhat unexpected, to discover that it is the non-spherical shape of the fluid molecule which provides the most significant of the anisotropic forces, and not the octopolar forces. Whilst the preferred proposed model (D) clearly does not provide the definitive intermolecular potential for CF_4, the stringent tests applied have demonstrated that for most practical purposes it may serve as a useful source of thermodynamic properties with acceptably good accuracy.

REFERENCES

[1] CALADO, J. C. G. and CLANCY, P., *Rev. Port. Quim*, **26**, 85 (1984).

[2] MAITLAND, G. C., RIGBY, M., SMITH, E. B. and WAKEHAM, W. A., *Intermolecular Forces,* Clarendon Press, Oxford, 1981.

[3] POWLES, J. G., EVANS, W. A., MCGRATH, E., GUBBINS, K. E. and MURAD, S., *Mol. Phys.*, **38**, 893 (1979).

[4] RUBIO, R. G., CALADO, J. C. G., CLANCY, P. and STREETT, W. B., *J. Phys. Chem.*, **89**, 4637 (1985).

[5] LOBO, L. Q., MCCLURE, D. W., STAVELEY, L. A. K., CLANCY, P., GUBBINS, K. E. and GRAY, C. G., *J. Chem. Soc. Fara. Trans. II*, **77**, 425 (1981).

[6] MACCORMACK, K. E. and SCHNEIDER, W. G., *J. Chem. Phys.*, **19**, 849 (1951).

[7] DOUSLIN, D. R., HARRISON, R. H., MOORE, R. T. and MCCULLOGH, J. P., *J. Chem. Phys.*, **35**, 1357 (1961).

[8] MONTAGUE, D. G., CHOWDURY, M. R., DORE, J. C. and REED, J., *Mol. Phys.*, **50**, 1 (1983).

[9] ASENBAUM, A. and WILHELM, E., *Adv. Mol. Relax. Int. Proc.*, **22**, 187 (1982).

[10] MONSON, P. A., *Mol. Phys.*, **47**, 435 (1982).

[11] GUBBINS, K. E. and TWU, C. H., *Chem. Eng. Sci.*, **33**, 863; 879 (1978).

[12] GRAY, C. G., GUBBINS, K. E. and TWU, C. H., *J. Chem. Phys.*, **69**, 182 (1978).

[13] CLANCY, P., GUBBINS, K. E. and GRAY, C. G., *Fara. Disc. Chem. Soc.*, **66**, 116 (1978).

[14] ANGUS, S., ARMSTRONG, B. and DE REUCK, K. M., *International Thermodynamic Tables of the Fluid State - 5, Methane* (Pergamon, Oxford, 1977).

[15] LOBO, L. Q. and STAVELEY, L. A. K., *J. Chem. Eng. Data*, **26**, 404 (1981).

[16] LUCAS, K., personal communication.