

Thermodynamic properties of CH₄, CCl₄ and CF₄ on the melting line. Theory and computer simulation

L.N. Yakub and E.S. Bodiul

*V.S. Martynovsky Institute of Refrigeration, Cryotechnology and Energetics,
Odessa National Academy of Food Technologies, Ukraine
E-mail: lydia.yakub@gmail.com*

Received October 24, 2018

Thermodynamic properties of the condensed phases of methane CH₄, carbon tetrafluoride CF₄ and carbon tetrachloride CCl₄ on the melting line and in the high-pressure region were studied using the equations of state developed earlier for methane in the framework of the thermodynamic perturbation theory. We also present the results of Monte Carlo computer simulations of fcc phases of methane, carbon tetrachloride, and of the monoclinic tetrafluoromethane phase using a potential model that takes into account both the central and octupole–octupole interaction. The contribution of the octupole–octupole interaction to the thermodynamic properties of crystals are evaluated. The simulation results are compared with the available experimental data on the sublimation and melting lines, as well as to results of previous calculations based on the equations of state.

Keywords: thermodynamic properties, methane, perturbation theory, Monte Carlo simulations, molecular crystals.

1. Introduction

Interest to molecular crystals composed of tetrahedral molecules of the type XY₄, where X is an element of the carbon group, and Y is a hydrogen isotope or halogen, has been around for a long time. The number of publications devoted to the study of the properties of these crystals in the high-pressure region is growing. In recent years, it has been established that methane CH₄ in a condensed state exists not only on Earth, but also on some planets of the Solar System [1].

Another area where the data on the thermodynamic properties of these crystals are important is the search for new energy-intensive molecular systems based on carbon materials suitable for storing and easy extraction of molecular hydrogen from them as fuel.

The solution of a number of problems in low-temperature engineering, thermal physics, astronomy is impossible without reliable information about the thermodynamic properties of methane and its halo derivatives. This requires knowledge of the thermodynamic properties of these substances at high pressures which is now possible only for simplest molecular solids and fluids like hydrogen [2]. For understanding the thermodynamic stability of binary mixtures consisting of compounds of carbon and hydrogen, knowledge of the properties and phase diagrams of such molecular crystals is very important [3–6].

Carbon tetrafluoride CF₄, is a molecular analog of methane, it attracts the attention of many researchers due to its simplicity and high symmetry of molecules. Interest in it is also explained by the fact that its commercial significance has recently been growing due to the development of dry etching technology in the microelectronic industry [4]. Carbon tetrafluoride is also a by-product of detonation and an understanding of its chemical and physical properties is crucial for modeling explosion processes.

At present, experimental studies of molecular crystals in the field of extreme state parameters in diamond anvils [7] are underway, but the limited possibilities of experimental studies at low temperatures and high pressures make the theoretical studies and simulations of the properties of methane and its derivatives. Unfortunately, such studies cannot yet satisfy all requests for the thermodynamic properties of methane, CCl₄ and CF₄ in a wide range of temperatures and pressures. To solve many practical problems, reliable equations of state are needed that adequately describe the thermodynamic properties of methane and its derivatives, both in the single-phase region and in the sublimation and melting lines.

The aim of this work is a theoretical study of the thermodynamic properties of molecular crystals: methane and its halogen derivatives, based on the use of theoretical equations of state (EOS) of CX₄ solids (X = H, F, Cl) [2].

To assess the quality of these EOS' in areas where there are no reliable experimental data, the direct calculations of the properties of the condensed phases of methane, CF₄, and CCl₄ were carried out using the Monte Carlo computer simulation method. Results of such simulations can be used to estimate the accuracy of theoretical predictions of properties in the high-pressure region.

The phase diagrams of methane, carbon tetrafluoride, and carbon tetrachloride discussed in [3–6], illustrate complexity of these crystals and the presence of many high-pressure phases. This poses sometimes complex tasks for theorists. The problem of the EOS development is usually solved for each phase of CH₄, CCl₄ and CF₄ individually.

An important task is to obtain the equation of state, which adequately describes the thermodynamic properties of molecular crystals not only on the sublimation line, but also at high pressures which is connected with the tasks of obtaining new energy-intensive substances, the problems of studying the earth's interior and the detection of methane on satellites of the planets of the solar system [1].

In this paper, we consider only those phases of the above-mentioned crystals, which are characterized by relatively free rotation of molecules and are bordered with a liquid on the phase diagrams.

The high-temperature phases of solid CCl₄, CBr₄, Cl₄ are, like in the case of methane, orientationally disordered and have an fcc lattice with four molecules per cell. But low-temperature phases often have other types of lattice structure [8].

Thus, carbon tetrachloride CCl₄ solidifies at the temperature of about 245 K in the fcc crystal structure (phase *Ia*), and then transforms into rhombohedral (phase *Ib*) [6]. The phase bordering on the liquid, has a fcc structure on the melting line, and practically free rotation of the molecules. The region near the melting line where this phase exists is rather narrow (from 245 to 320 K) and both direct and reverse transitions to the liquid phase take place here [9].

In the group of halomethanes, carbon tetrafluoride CF₄ differs by a relatively low melting point and a monoclinic structure of the high-temperature phase. Tetrafluoromethane has its melting point at $T = 89.2$ K, which is 1.2 K below the melting point of methane, and its parameters such as mass, moment of inertia and octupole moment are significantly higher than those of methane. It was found that, in the β phase, at a temperature of 77 K, it has a monoclinic structure with parameters [8]: $a = 13.732$ Å, $b = 12.815$ Å, $c = 13.429$ Å, $\alpha = 93.6^\circ$, which differs only slightly from the structure characteristic of the solidified methane phase.

An analysis of the structures of molecular crystals formed by tetrahedral molecules was performed in [10], where authors suggested that halomethanes, by analogy with deuteromethane, can be considered like pure methane under high pressure.

2. Equation of state for molecular crystals CH₄, CCl₄ and CF₄

Among the many simple molecular crystals, solidified methane and its halide derivatives are closest to the model of spherical molecules, since the tetrahedral shape of methane molecules is very close to spherical. The non-central contribution to the interaction in the condensed state may have little effect on the behavior of crystalline methane. If we consider the multipole expansion, then for the molecules of these crystals the main contribution of non-central forces is their octupole–octupole interaction, and all contributions (hexadecapole, *etc.*) do not make a significant contribution to the thermodynamic properties of methane and its halogen-substituted like CCl₄ and n CF₄ [11].

Due to the relative weakness of this interaction, the high-temperature phase of solid methane is similar in its properties to solidified inert gases. It allows applying in prediction of thermodynamic properties of methane the thermodynamic perturbation theory (TPT), where a system of spherical molecules is a zero approximation and the octupole–octupole interaction of methane molecules is as a perturbation [12].

The free energy of the solid phase is represented as

$$F(V, T) = F^{(0)}(V, T) + \Delta F_{\text{Oct}}, \quad (1)$$

where $F^{(0)}(V, T)$ is Helmholtz free energy of a crystal consisting of spherical molecules, and F_{Oct} is TPT correction for octupole–octupole interactions [13].

The method that underlies the construction of the basic equation for Helmholtz free energy $F^{(0)}(V, T)$ implicitly takes into account both the anharmonicity of oscillations and the double and triple correlations between particle displacements [14].

For practical calculations in this work we used an analytical approximation of the canonical equation for Helmholtz free energy of crystalline phase of highly anharmonic crystal in the form proposed in [15]:

$$f(\rho^*, T^*) = u^{(0)}(\rho^*) - \frac{3}{2} T^* \ln T^* - \sum_{n=0}^{n_{\max}} \sum_{m=2}^{m_{\max}} \frac{a_{nm}}{m-1} \rho^{*n} T^{*m} + T^* \sum_{n=0}^3 \frac{b_n}{n+1} \rho^{*n+1} + c T^*. \quad (2)$$

Here $f = F^{(0)}/\varepsilon$, $T^* = kT/\varepsilon$ and $\rho^* = N\sigma^3/V$ are free energy, temperature and density, reduced to Lennard-Jones potential parameters, b_n and a_{nm} ($n = 0, \dots, n_{\max}$; $m = 2, \dots, m_{\max}$), $n_{\max} = 2$, $m_{\max} = 5$ are parameters defined by fitting the computer simulation data for the Lennard-Jones fcc crystal.

Within the framework of TPT, the correction for octupole–octupole interaction is written as

$$\Delta F_{\text{oct}} = \langle \Delta U_{\text{oct}} \rangle - \frac{1}{2kT} \left[\langle \Delta U_{\text{oct}}^2 \rangle - \langle \Delta U_{\text{oct}} \rangle^2 \right] + \dots \quad (3)$$

Here the angle brackets mean the averaging of the energy of the octupole–octupole interaction of molecules by orientations over the distribution function of the reference system with the central interaction. Averaging over orientations can be carried out in the same way as for the system of free rotors [13]. In this case, the multipole symmetry of non-central interaction leads to the fact that the first-order correction vanishes. In view of this, the influence of the non-sphericity of the interaction potential on the thermodynamic properties of the system is given by the mean value of the squared octupole–octupole interaction.

As a result, for the dimensionless (*i.e.*, reduced using the Lennard-Jones potential parameters ε and σ) for the octupole–octupole contribution to the Helmholtz free energy, one obtains the following expression:

$$\left\langle \left(\Delta U_{\text{oct}}^* \right)^2 \right\rangle = 1.863 S_{14} \Omega^{*4} \rho^{*14/3}, \quad (4)$$

where S_{14} is the so-called lattice sum [16], Ω^* is the reduced octupole moment of the molecule, and ρ^* is the reduced density.

Using this expression, we can approximately calculate contributions of the octupole–octupole interaction to all thermodynamic functions. The corresponding kinetic contribution due to the free rotation of molecules should also be included in the equation of state. Therefore to calculate thermodynamic properties of a solid from equations (1)–(4) one only needs to know three parameters: two parameters of the Lennard-Jones potential and the octupole moment.

Note that the equation of state used in the paper does not take into account quantum effects and hence was used to calculate the thermodynamic properties of methane at relatively high temperatures (from $T = 50$ K). In the thermodynamic properties of all heavier halogen-substituted methane, such as CF_4 and CCl_4 , at such temperatures quantum effects are not noticeable.

3. Computer simulation of methane and its derivatives

We performed Monte Carlo computer simulation of crystalline phases of CH_4 , CCl_4 , and CF_4 using the same potential interaction model that was adopted in deriving the above equation of state. The results of our Monte Carlo simulations were compared with the results of calculations using EOS, aiming to estimate the correctness of the octupole–octupole interaction contributions, calculated using TPT. These simulations made it also possible checking the ability of the proposed TPT-based EOS to predict thermodynamic properties of these phases in the absence of experimental data.

To solve these problems, a Monte Carlo simulation program based on the classic Metropolis algorithm and periodic boundary conditions was developed. The program allows

direct calculation of the thermodynamic properties of the crystalline phases of methane and its derivatives. The essence of the algorithm of its work is as follows.

We used the following expression for the pair-additive potential energy of a system of N molecules:

$$U_N = \sum_{1 \leq i < j \leq N} \Phi(\mathbf{R}_i, \mathbf{R}_j). \quad (5)$$

Here $\Phi(\mathbf{R}_i, \mathbf{R}_j)$ is the energy of pair interaction between CX_4 molecules:

$$\Phi(\mathbf{R}_i, \mathbf{R}_j) = \Phi(|\mathbf{R}_i - \mathbf{R}_j|) + V_{\Omega\Omega}(\mathbf{R}_i, \mathbf{R}_j), \quad (6)$$

where $\Phi(r)$ is the central Lennard-Jones potential

$$\Phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (7)$$

The potential parameters ε and σ are, respectively, the depth of the potential well and the characteristic diameter of a molecule.

The additional term $V_{\Omega\Omega}(\mathbf{R}_i, \mathbf{R}_j)$ takes into account the non-central octupole–octupole interaction of molecules. The exact expression obtained in [11] was used for its analytical representation:

$$V_{\Omega\Omega}(\mathbf{R}_i, \mathbf{R}_j) = -\frac{12 \Omega^2}{5 R^7} \{693 K_1 K_2 - 63B + 7C - D\}. \quad (8)$$

Here Ω is octupole moment of molecules, \mathbf{R} is the distance between their centers,

$$\begin{aligned} K_1 &= (\mathbf{R}_0 \cdot \mathbf{e}_{1x})(\mathbf{R}_0 \cdot \mathbf{e}_{1y})(\mathbf{R}_0 \cdot \mathbf{e}_{1z}), \\ K_2 &= (\mathbf{R}_0 \cdot \mathbf{e}_{2x})(\mathbf{R}_0 \cdot \mathbf{e}_{2y})(\mathbf{R}_0 \cdot \mathbf{e}_{2z}), \end{aligned} \quad (9)$$

where \mathbf{e}_{ik} ($i = 1, 2$; $k = x, y, z$) are unit vectors that determine the orientation of molecules, \mathbf{R}_0 is the unit vector of intermolecular axis. For the exact expressions for B , C and D we refer to the original work of Isnard *et al.* [11].

A definite number N of CX_4 molecules ($X = \text{H}, \text{F}, \text{Cl}$) were initially placed in the sites of the crystal lattice inside the main Monte Carlo cell, their orientations were set randomly. Molecules CX_4 were considered rigid. To specify their position and orientation, six variables were used: three spatial (Cartesian coordinates x, y, z of the center of mass) and three Eulerian angles (θ, ϕ, ψ) determining the orientation of the tetrahedral molecule.

After placing the molecules in the cell, the process of consecutive moving of molecules was started. Molecules were chosen randomly and attempts were made to move selected molecules to their new positions (the molecule was shifted and simultaneously rotated). The process of individual molecules moving was realized in such a way, that selected molecules were given small random shifts of each of spatial variables (six random numbers were generated accordingly). The well-known moves accepting or rejecting rules of Metropolis [17] was applied.

The interval of possible displacements was specified for angular and spatial displacements. These values were selected in such a way that the share of successful movements was about 40%.

Simulations were performed within the NVT ensemble for different N depending on the crystal lattice type and cell size: from $N = 128$ for the monoclinic structure $Fm3n$ to $N = 256$ for the fcc lattice. No special restrictions ensuring the preservation of the crystal structure in the process of computer experiment were introduced. Therefore, it was important to control that the original structure of the crystal is preserved.

After 20,000–30,000 successful steps, a steady state was established, then approximately every 1,500 steps the pressure, internal energy, heat capacity, thermal pressure, and isothermal compressibility coefficient were calculated and stored in a file for further analysis and processing. Results were averaged over approximately 60,000 consecutive successful steps. After a certain number of steps (approximately 2–3 successful displacements on average per atom), the internal energy and pressure from virial theorem as well as heat capacities and thermal coefficients were calculated.

4. Results and discussion

The developed Monte Carlo calculation program was first applied to study the thermodynamic properties of crystals: the high-temperature, fcc phase of methane and carbon tetrachloride, first, and then also the monoclinic structure of carbon tetrafluoride.

To calculate thermodynamic properties either of the two methods (EOS or Monte Carlo) requires the Lennard-Jones potential parameters ε и σ , as well as the octupole moment Ω .

In this study the Lennard-Jones potential parameters were not fitted to the experimental data, but taken from the literature. For methane, the following values were accepted [18], $\varepsilon/k = 148$ K, $\sigma = 3.77$ Å. These parameters were found from the second virial coefficient and viscosity of a high-temperature gas, where the interaction effect octupole–octupole is small. The magnitude of the octupole moment CH₄ ($\Omega = 4.5 \cdot 10^{-34}$ esu·cm³) was adopted from [19]. As in the case of methane, we adopted the Lennard-Jones potential parameters for CF₄: $\varepsilon/k = 141$ K, $\sigma = 4.63$ Å, and $\Omega = 4.44 \cdot 10^{-34}$ esu·cm³ known in the literature [20]. The parameters for CCl₄ $\varepsilon/k = 327$ K, $\sigma = 5.22$ Å, $\Omega = 15 \cdot 10^{-34}$ esu·cm³ were determined from data presented in [19].

We attempted to predict the properties of methane, carbon tetrafluoride, and carbon tetrachloride in their sublimation and melting lines. In this work, we considered the fcc phase I of methane and phase Ia of carbon tetrachloride, as well as the monoclinic β phase of tetrafluoromethane [8], which are stable and reversibly transforms into the liquid phase at higher temperatures [3,4,6].

For solid methane, calculations were performed on the melting line at eight temperatures and experimental densi-

ties [21]. For solid CCl₄, Monte Carlo simulation was performed along the melting line of the fcc phase Ia from 245 to 320 K [9]. For solid CF₄, Monte Carlo simulations were performed for on sublimation line and the melting lines.

The most important is the comparison of the calculation results with experimental data. Comparison of the thermodynamic properties of methane (molar volume, linear expansion coefficient, compressibility and heat capacity) calculated by the state equation on the sublimation line with experimental data [22] was carried out in [23].

In [12], we estimated the possibilities of the equation of state in the high-pressure region when calculating the melting line of methane. The data given in Table 1 allows us to estimate the possibilities of the proposed equation of state in the high-pressure region by comparing with computer simulation data. It can be noted that there is good agreement between the calculation and the machine experiment, both for pressure and for thermal coefficients (thermal expansion α_P , and isothermal compressibility β_T).

Table 1. Thermodynamic functions of solid methane on its melting line. Comparison of the Monte Carlo simulation (MC) and equation of state (EOS) results

T , K	P , GPa	Method	V , cm ³ /mole	α_P , 10 ⁻³ K ⁻¹	β_T , GPa ⁻¹
90.7	0.008	MC	32.87	1.896	0.907
		EOS	32.81	1.716	0.835
111.3	0.087	MC	31.75	1.295	0.642
		EOS	31.80	1.236	0.605
131.8	0.186	MC	30.92	1.144	0.535
		EOS	30.88	0.943	0.460
156.97	0.323	MC	29.97	0.797	0.396
		EOS	29.87	0.715	0.346
180.36	0.465	MC	29.09	0.614	0.310
		EOS	29.04	0.575	0.276
212.85	0.677	MC	28.16	0.453	0.238
		EOS	28.02	0.444	0.211
237.58	0.866	MC	27.47	0.388	0.201
		EOS	28.18	0.374	0.177
260.85	1.034	MC	26.88	0.347	0.176
		EOS	26.74	0.323	0.152

The assessment of the reliability of Monte Carlo is illustrated in Fig. 1, where the simulation results for pressure as function of molar volume are compared with experimental data of Cheng [21] and Abramson [7]. Unfortunately, there are no experimental values of density above 300 K; therefore, no comparison was made in this area. However, the comparison made in Fig. 1 confirms the conclusion that the potential model used in the Monte Carlo method and the simulation performed provide good accuracy of the predicted specific volume of methane at high pressures and temperatures.

Thus, the comparison performed demonstrates the ability to use machine experiment data to evaluate the results

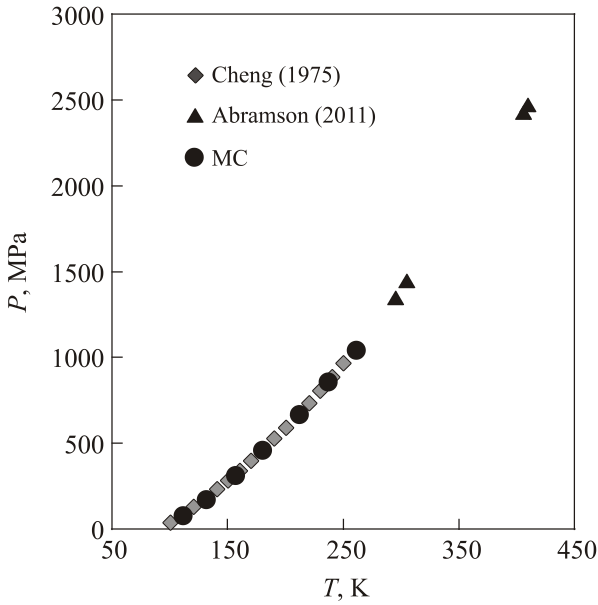


Fig. 1. Pressure of crystalline methane on the melting line. Comparison Monte Carlo simulation results (circles) with experimental data of Cheng [21] (diamonds) and Abramson [7] (triangles).

of the calculation of thermodynamic properties using the proposed equation of state. Our research results confirm this observation.

In Fig. 2 we compare the temperature dependence of the isothermal compressibility on the melting line of solid methane determined in the work using two methods: EOS and Monte Carlo computer simulation.

The relative contribution of the octupole–octupole interaction to the thermodynamic functions of solid methane was previously estimated [12] using equation of state. The corre-

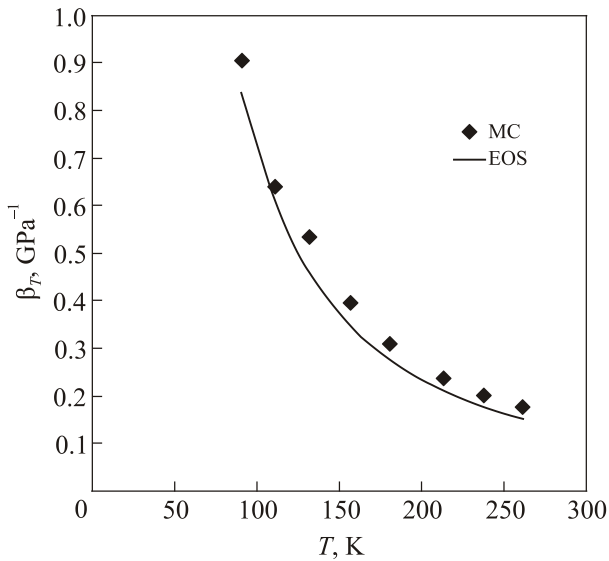


Fig. 2. Temperature dependence β_T of isothermal compressibility of solid methane on its melting line. Comparison of calculations based on EOS and Monte Carlo simulation.

sponding contributions to pressure, to coefficients of volume expansion and compressibility, as well as to the excess heat capacity of methane, calculated by the Monte Carlo method, are presented in Table 2. They are in good agreement with our previous estimates [12].

Table 2. Relative contributions of the octupole–octupole interaction to pressure P , isothermal compressibility α_P and thermal expansion β_T coefficients, and excess heat capacity ΔC_V on the melting line of methane. Monte Carlo simulation results

T, K	$\delta P, \%$	$\delta\alpha_P, \%$	$\delta\beta_T, \%$	$\delta\Delta C_V, \%$
90.7	–	27.5	9.5	43.9
111.3	–15.0	20.1	6.5	30.1
131.8	–8.1	15.0	5.1	22.3
156.97	–3.4	11.1	3.0	18.0
180.36	–1.9	6.2	1.0	14.9
212.85	–1.3	2.7	–0.4	12.4
237.58	–1.2	4.0	0.5	10.1
260.85	–0.9	8.2	1.7	12.2

During the Monte Carlo simulation of high-temperature phase CF_4 and CCl_4 and calculation of thermodynamic properties using EOS on their sublimation and melting lines information about the structure of the phases is required. The data on the parameters of the CF_4 monoclinic phase structure used in this work were taken from [8]. In the phase adjoining the liquid, where the rhombohedral structure is observed, Monte Carlo calculations for this structure were not carried out.

The comparison of the molar volumes of CF_4 calculated on the sublimation lines by the Monte Carlo method with experimental data [8,24] is shown in Fig. 3. Molar volumes

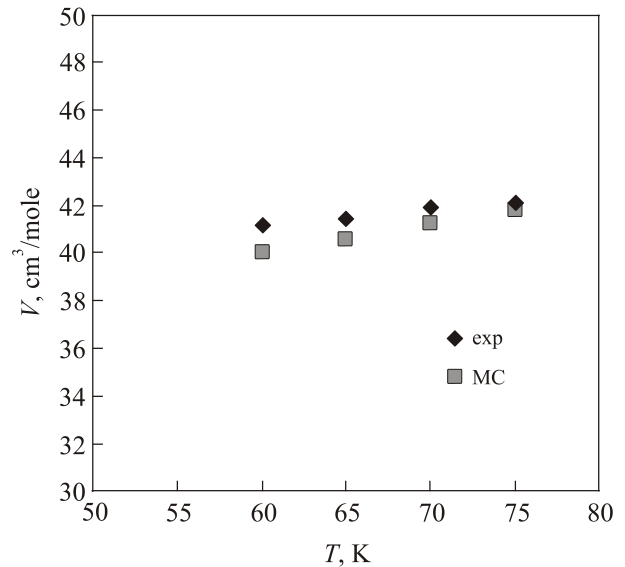


Fig. 3. Molar volume of solid tetrafluoromethane CF_4 on the sublimation line. Comparison of the Monte Carlo simulation results (squares) with experimental data [8,24] (diamonds).

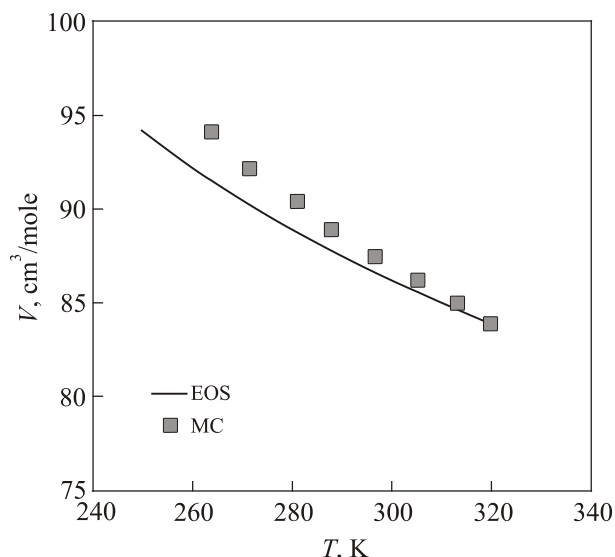


Fig. 4. Molar volume of solid carbon tetrachloride CCl₄ on the melting line. Comparison of the Monte Carlo simulation (squares) data and EOS results (solid line).

corresponding to zero pressure at which the Monte Carlo simulation was performed were estimated using calculated isothermal compressibility values. Our results are in reasonable agreement with the available experimental data. Noticeable deviations of the calculation from the experimental data are observed only at temperatures below 65 K.

Unfortunately experimental values of the CCl₄ solid phase density are absent in literature available. Nevertheless it is possible to compare the calculated volumes obtained using the theoretical equation of state and computer simulation (Fig. 4). Since in the Monte Carlo method requires that the volumes are specified, we were forced to fit the values of volumes to obtain correct pressure on the melting line. The corresponding molar volumes, as in the case of CF₄, were estimated using calculated values of isothermal compressibility.

The results of the thermodynamic properties calculations using equation of state and Monte Carlo computer simulation also agree well. Considering the use of the same potential model, it can be stated that the proposed form of the equation of state is correct. The octupole–octupole interaction of molecules at elevated temperatures makes only a small contribution to thermodynamic functions, but at low temperatures it becomes significant.

In conclusion, it should be noted that for the extension of the methods used in this work (the canonical EOS and Monte Carlo) to other non-cubic crystal structures is possible, but it requires additional efforts.

1. E.R. Stofan, C. Elachi, J.I. Lunine, R.D. Lorenz, B. Stiles, K.L. Mitchell, S. Ostro, L. Soderblom, C. Wood, H. Zebker, S. Wall, M. Janssen, R. Kirk, R. Lopes, F. Paganelli, J. Radebaugh, L. Wye, Y. Anderson, M. Allison, R. Boehmer, P. Callahan, P. Encrenaz, E. Flamini, G. Francescetti, Y. Gim, G. Hamilton, S. Hensley, W.T.K. Johnson, K. Kelleher, D. Muhleman, P. Paillou, G. Picardi, F. Posa, L. Roth, R. Seu, S. Shaffer, S. Vetrella, and R. West, *Nature* **445**, 61 (2007).
2. E.S. Yakub, *Int. J. Thermophys.* **22**, 505 (2001).
3. R. Bini and G. Pratesi, *Phys. Rev. B* **55**, 14800 (1997).
4. H.E. Lorenzana, M.J. Lipp, W.J. Evans, and N. Hemmi, *J. Low Temp. Phys.* **122**, 279 (2001).
5. R.G. Ross and P. Andersson, *Mol. Phys.* **36**, 39 (1978).
6. V.E. Bean and S.D. Wood, *J. Chem. Phys.* **72**, 5838 (1980);
7. E.H. Abramson, *High Pressure Research* **31**, 549 (2011).
8. N.A. Klimenko, N.N. Gal'tsov, and A.I. Prokhvatilov, *Fiz. Nizk. Temp.* **34**, 1212 (2008) [*Low Temp. Phys.* **34**, 960 (2008)].
9. M. Maruyama, K. Kawabata, and N. Kuribayashi, *J. Cryst. Growth* **220**, 161 (2000).
10. A.I. Prokhvatilov, N.N. Galtsov, N.A. Klimenko, and M.A. Strzhemechny, *Fiz. Nizk. Temp.* **34**, 185 (2008) [*Low Temp. Phys.* **34**, 142 (2008)].
11. P. Isnard, D. Robert, and L. Galatry, *Mol. Phys.* **31**, 789 (1976).
12. L.N. Yakub and O.S. Bodiul, *J. Low Temp. Phys.* **187**, 33 (2017).
13. M.S. Ananth, K.E. Gubbins, and C.G. Gray, *Mol. Phys.* **28**, 1005 (1974).
14. L. Yakub and E. Yakub, *J. Chem. Phys.* **136**, 144508 (2012).
15. L. Yakub, *Int. J. Thermophys.* **35**, 1957 (2013).
16. R.D. Misra and M. Born, *Proc. Camb. Phys. Soc.* **36**, 173 (1940).
17. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
18. P.M. Kessel'man, V.R. Kamenetskii, and E.S. Yakub, *Transport Properties of Real Gases*, Vishcha Shkola, Odessa (1976) [in Russian].
19. D.E. Stogryn and A.P. Stogryn, *Mol. Phys.* **11**, 371 (1966).
20. H. Enjkido, T. Shinoda, and Y. Mashiko, *Bull. Chem. Soc. Jpn.* **42**, 3415 (1969).
21. M. Cheng, W.B. Daniels, and R.K. Crawford, *Phys. Rev. B* **11**, 3972 (1975).
22. A.I. Prokhvatilov and A.P. Isakina, *Fiz. Nizk. Temp.* **9**, 419 (1983) [*Sov. J. Low Temp.* **9**, 213 (1983)].
23. L.N. Yakub and O.S. Bodiul, *Refriger. Eng. Technol.* **52**, 80 (2016).
24. D.N. Bol'shutkin, V.M. Gasan, A.I. Prokhvatilov, and A.I. Erenburg, *Acta Cryst. B* **28**, 3542 (1972).

Термодинамічні властивості CH_4 , CCl_4 та CF_4
на лінії плавлення. Теорія та комп'ютерне
моделювання

Л.М. Якуб, О.С. Бодюл

Термодинамічні властивості конденсованих фаз метану CH_4 , тетрафторметану CF_4 та чотирихлористого вуглецю CCl_4 вивчалися на лінії плавлення та в області високого тиску з використанням рівнянь стану, розвинених раніше для метану в рамках термодинамічної теорії збурень. Представлено результати комп'ютерного моделювання Монте-Карло ГЦК фаз метану та чотирихлористого вуглецю, а також моноклінної фази тетрафторметану з використанням моделі потенціалу, що враховує як центральну, так і октупольно–октупольну взаємодію. Оцінюється внесок октупольно–октупольної взаємодії в термодинамічні властивості кристалів. Результати моделювання порівнюються з наявними експериментальними даними на лініях сублімації та плавлення, а також з результатами попередніх розрахунків, заснованих на рівняннях стану.

Ключові слова: термодинамічні властивості, метан, теорія збурень, метод Монте-Карло, молекулярні кристали.

Термодинамические свойства CH_4 , CCl_4 и CF_4
на линии плавления. Теория и компьютерное
моделирование

Л.Н. Якуб, Е.С. Бодюл

Термодинамические свойства конденсированных фаз метана CH_4 , тетрафторметана CF_4 и четыреххлористого углерода CCl_4 изучались на линии плавления и в области высокого давления с использованием уравнений состояния, развитых ранее для метана в рамках термодинамической теории возмущений. Представлены результаты компьютерного моделирования Монте-Карло ГЦК фаз метана и четыреххлористого углерода, а также моноклинной фазы тетрафторметана с использованием модели потенциала, учитывающей как центральное, так и октупольно–октупольное взаимодействие. Оценивается вклад октупольно–октупольного взаимодействия в термодинамические свойства кристаллов. Результаты моделирования сравниваются с имеющимися экспериментальными данными на линиях сублимации и плавления, а также с результатами предыдущих расчетов, основанных на уравнениях состояния.

Ключевые слова: термодинамические свойства, метан, теория возмущений, метод Монте-Карло, молекулярные кристаллы.