Features of the thermodynamic properties of gaseous and solid methane

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Abstract. A detailed analysis and calculation of the rotational component of the heat capacity of gaseous and solid methane is carried out. Correction of the generally accepted estimates of the contribution of quantum effects to the rotational heat capacity of methane in both gaseous and solid state is performed.

1. Introduction
In recent years, there has been a sharp increase in interest in solid methane. In particular, it proved to be the best moderator of cold neutrons in pulsed nuclear power sources, it is widely distributed on Saturn, Jupiter and their satellites; it is one of the cryocrystals possessing a wide spectrum of physical properties. The range of properties is so wide that some reference books on the properties of cryocrystals [1] ignored the completely exceptional experimental data on solid methane in temperature range 65-70 K. Some experimental data in this temperature range have not yet been properly interpreted theoretically.

2. Results and discussion
In a remarkable experimental work by Tomita [2], it was found that a sharp change in the nature of the rotations of solid methane molecules occurs at a temperature of about 65 K. This fact is extremely surprising. First of all, the fact of the existence of rotation of methane molecules in the solid phase, in spite of the very likely inhibition of molecular rotations due to the “ears”, is surprising. If we start from the hypothesis that the anomalies are associated with the rotation of molecules, then the only feature of the rotational component of the heat capacity is the nonmonotonicity of its temperature dependence. There is a point of maximum heat capacity at a temperature of order

\[ T_{\text{rot}} = \frac{h^2}{2kT} \]

where \( k \) is the Boltzmann constant.

First, we calculate the rotational temperature \( T_{\text{rot}} \) from the known parameters of the methane molecule using formula (1). The moment of inertia of a spherical top is determined by the relation [3, 4].
\[ I = ma^2 = \frac{8}{3}ml^2 \]  

(2)

where \( m \) is the proton mass, \( a \) is the distance between the hydrogen atoms in the methane molecule, and \( l = 1.093 \times 10^{-10} \text{m} \) is the length of the bond between the carbon and hydrogen atoms. As a result, we find the moment of inertia of the methane molecule

\[ I = 5.324 \times 10^{-47} \text{kg} \cdot \text{m}^2. \]  

(3)

This is in agreement with the experimental value of the moment of inertia of methane \( 5.17 \times 10^{-47} \text{kg} \cdot \text{m}^2 \)\footnote{[5]}. Substituting (3) into (1), we obtain the value of the rotational temperature of methane

\[ T_{\text{rot}} = 7.57 \text{ K}. \]  

(4)

The physical meaning of the rotational temperature is the temperature at which quantum effects begin to manifest themselves clearly in the rotational degrees of freedom of methane molecules.

Note that the effect detected by Tomita occurs at temperatures that are an order of magnitude higher than the rotational temperature of gaseous methane of 7.5 K. In other words, \( T=60 \text{ K} \) lies in the temperature range at which the rotational degrees of freedom of the methane molecules seemingly, must obey classical statistics. Therefore, in this temperature range it was initially difficult to expect the manifestation of quantum effects in rotational degrees of freedom.

Nevertheless, a hypothesis was proposed in \footnote{[6]} that the feature observed by Tomita is related to the manifestation of the quantum nature of the rotational degrees of freedom of methane molecules in the crystalline state. The rotation of molecules in the solid state is possible due to the tunnel effect \footnote{[7]}, therefore, in formula (1), instead of the moment of inertia of the methane molecule, the effective moment of inertia of elementary excitations corresponding to the collectivization of rotational degrees of freedom of methane molecules should enter. Since the moment of inertia of elementary excitations (topons) is an order of magnitude much smaller than the moment of inertia of the methane molecule.

In this case, the rotational component of the thermodynamic functions of solid methane is described in the framework of the model of an ideal gas consisting of topon quasiparticles. The thermodynamics of an ideal quantum gas with rotational degrees of freedom of molecules was created in the late 1920s \footnote{[8]}. The rotational component of the heat capacity of an ideal gas consisting of topos is a function of the dimensionless temperature

\[ C_{\text{rot}} = f(\tau), \quad \tau = \frac{T}{T_{\text{rot}}}. \]  

(5)

To calculate the temperature dependence of the rotational heat capacity of methane, it is required to find the corresponding partition function

\[ Z = \sum_{n=0}^{\infty} g_n e^{-\frac{n(n+1)}{\tau}}, \]  

(6)

where \( g_n \) is the multiplicity of the degeneracy of the \( n \)-th state of the top, \( \tau \) is the dimensionless temperature determined by the relation (5).

The whole specificity of the thermodynamics of a particular ideal quantum gas in terms of a dimensionless temperature lies in the nature of the dependence of the degeneracy multiplicity of a top on its state number. In contrast to other degrees of freedom, the rotational component of the heat capacity is a nonmonotonic function of temperature: before rushing to zero at \( T \to 0 \), the rotational heat capacity increases to a certain maximum value at \( T=T_0 \) and only then rushes to zero. The value of the rotational heat capacity at the maximum point is greater than its classical value, which is reached at
Before analyzing the thermodynamic properties of crystalline methane in the framework of the topon model, we will discuss the current state of the theory of ideal methane gas. Note that the theoretical calculations of the rotational component of the heat capacity of methane, carried out by different authors [10, 11, 12], significantly contradict each other. The results of these calculations are partially given in the monographic and educational literature [9, 13].

The type of connection between the degeneracy multiplicity and the state number of the top depends on the symmetry type of the spherical top, and the type of symmetry is predetermined by the internal degrees of freedom of the top.

The multiplicity of degeneracy of polyatomic molecules with large spins of identical nuclei can be calculated from the formula [14]

\[ g_n = (2n+1)^2. \]  (7)

In this case there are two types of degeneracy, each of which has multiplicity \( g = 2n+l \). The first is connected with different directions of the angular momentum with respect to the molecule, and the second - with different directions of the angular momentum in space [14, 15].

However, methane is a spherical top because of its symmetry and also has small spins of identical nuclei. Therefore, methane exists in the form of three different spin-modifications \( 5A_e, 1E, 3F_e \), each of which is characterized by its rotational partition function [12, 14, 15, 16]. A simple formula of the type (7) for calculating the degeneracy multiplicities does not exist in this case. Only the first few terms in the low-temperature expansion of the statistical sum of methane are taken into account with allowance for all three spin-modifications [9, 15]. Moreover, the transition probabilities between different spin-modifications are extremely small, therefore, the real mixtures of modifications are usually nonequilibrium.

Using the first few terms in the expansion of the partition function of the methane with all three spin modifications, we obtain [1, 11]

\[
Z = 5 + 9e^{-\frac{1}{\tau}} + 25e^{-\frac{2}{\tau}} + 77e^{-\frac{4}{\tau}} + 117e^{-\frac{12}{\tau}} + \cdots. \]  (8)

In this expansion, terms are represented up to \( n=4 \). This expression is applicable only for \( T \leq T_0 \). Outside the low-temperature region (i.e., at \( T \geq T_0 \)), the omitted terms do not decrease as fast as the stored ones, and they can be taken into account in a rather rough approximation (7), which is applicable only for large \( n \) values [14]. As a result, we obtain the following expression for the partition function

\[
Z = \left[ 5 + 9e^{-\frac{1}{\tau}} + 25e^{-\frac{2}{\tau}} + 77e^{-\frac{4}{\tau}} + 117e^{-\frac{12}{\tau}} \right] + \sum_{n=5}^{\infty} (2n+1)^2 e^{-\frac{n(n+1)}{\tau}}. \]  (9)

The heat capacity of methane is found using the relation

\[
\tilde{N} = \beta^3 \frac{\partial^2 \ln Z}{\partial \beta^2}, \quad \beta = \frac{1}{\tau}. \]  (10)

The results of numerical calculations of the dependence of the rotational component of the heat capacity of methane on temperature are presented in Figs. 1, 2.

In all calculations, a characteristic maximum of the specific heat capacity is observed, but the value of \( T_0 \) is very sensitive to the form of the dependence of the degeneracy multiplicity on \( n \). In particular, replacing expression (7) by (8) at the same value of the rotational temperature of the ball top changes
the value of $T_0=0.59$ by 3, i.e. approximately 5 times. And the reason for this is only that these two tops differ from one another in symmetry properties.

Figure 1. The rotational heat capacity of a spherical top with degeneracy multiplicity $g_n = (2n+1)$.

Figure 2. The rotational heat capacity of methane with only the first five terms of the low-temperature expansion (8) of the partition function (curve C) taken into account, and with compensation of the discarded terms in approximation (7) (curve B).

As is known, an arbitrarily small distortion of a spherical top results in a violation of its symmetry and a sudden change in the partition function for the gas [15]. For example, if a methane molecule is transformed into an asymmetric top with a point symmetry $D_{2h}$ as a result of distortion of the configuration, then the first terms of the low-temperature expansion of the rotational partition function have the form [15]
We substitute this expression in place of (8) in (9) and find the corresponding temperature dependence of the heat capacity. The results of the numerical calculation are shown in Fig. 3.

Figure 3. Heat capacity versus temperature for two variants of the low-temperature part of the expansion of the partition function: curve (B) corresponds to formula (8), curve (C) - to formula (11).

Thus, the heat capacity of an ideal gas consisting of spherical-top type molecules as a function of the dimensionless temperature has a maximum point, the position of which depends very substantially on the type of symmetry of the top.

It is significant that the experimental determination of the maximum of the rotational heat capacity of real gaseous methane is very complicated by at least two circumstances.

1. The long duration of the establishment of thermodynamic equilibrium in a mixture of spin modifications of methane because of the extremely small probabilities of the transitions between these modifications [14].

2. Even a negligible distortion of the spherical top results in a sudden change in the partition function. The reasons for the distortion are abound - from inherent intermolecular interactions, to background electromagnetic radiation.

In connection with this, it is unlikely to expect any reproducibility of the results of an experimental study of the low-temperature heat capacity of methane in the gaseous state.

Unfortunately, this important conclusion is absolutely absent even in the literature of recent years, including Landau books.

Let us now turn to the thermodynamics of crystalline methane. Tomita [2] interpreted a sharp change in the character of the rotation of solid methane molecules in the temperature range 60-65 K as a result of a 20-fold change in the height of the barrier, which must be overcome by rotating molecules. The hypothesis of the rotation of methane molecules in the solid phase has not only experimental [2], but also theoretical justification [7]. It is pertinent to note here that Pauling [7] showed that in some molecular crystals (including, for example, CH₄, N₂, O₂), with an increase in temperature up to the melting point, the vibrational degrees of freedom of molecules can be transformed into rotational degrees of freedom. This is due, in particular, to the thermal expansion of solids.
In [6] it was assumed that in solid methane, instead of independent rotation of individual molecules characteristic of the gas phase, collective excitations of the rotational degrees of freedom of molecules should be considered because of the intermolecular interaction. Such a representation is in agreement with the results of Pauling [7] and is applicable at temperatures between the phase transition point (about 20 K) from the low-temperature cubic phase to the orientation-disordered phase along the hydrogen atoms of the fcc phase, and the melting point.

The corresponding quasiparticle (topon) is characterized by a single parameter - the effective moment of inertia. In contrast to the methane molecule, the topon is a spherical top not because of its symmetry, and therefore the multiplicity of the degeneracy of the rotational levels of the topon is determined by the formula (7). Then the graph of the temperature dependence of the heat capacity has the form shown in Fig.1.

Identifying the temperature of a sharp change in the character of the rotation of methane molecules with the maximum heat capacity of methane established by Tomita, we find a rough estimate of the rotational temperature of the topon $T_{rot} \approx 100$ K, i.e. the rotational temperature of topons is about 13 times higher than the rotational temperature of methane molecules in the gas phase. This means that solid methane in the entire temperature range of existence is a quantum cryocrystal.

It is interesting to note that solid methane exhibits anomalies in a number of physical properties of crystalline methane in the temperature range 60-65 K: a sharp change in the nature of the rotation of molecules [2]; temperature dependence of the molar volume [1]; coefficient of thermal expansion [1]; longitudinal and transverse ultrasound velocity [17]; low-frequency internal friction [18]; plasticity [18]; adhesion [19], radiolysis of defects at a neutron source [20], etc. These anomalies can be interpreted within the framework of the concept of collectivization of the rotational degrees of freedom of methane molecules in the solid phase [6, 21].

3. Conclusion
The temperature dependence of the heat capacity of methane in the gas phase is calculated and refined. It is shown that, because of the symmetry properties of the methane molecule, the quantum region of the heat capacity of gaseous methane exceeds its rotational temperature by an order of magnitude.

It is shown that solid methane in the entire temperature range of existence is a quantum cryocrystal.

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