Second Virial Coefficient of CH$_4$ Vapor in 5 mK–10000 K Temperature Range in Quantum and Classical Regimes

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The aim of this work is to study the second virial coefficient $B$ of methane (CH$_4$) vapor over a wide temperature range, $T = 5$ mK–10000 K. The coefficient is calculated in two temperature regions. First, for $T = 5$ mK–20 K — the quantum second virial coefficient $B_q$ is determined for the first time. It is found that the behavior of $B_q$ is similar to that of the CH$_4$–CH$_4$ potential. Standard expressions are then used in this quantum regime at the number density $n = 1 \times 10^{-4}$ Å$^{-3}$ to compute other thermodynamic properties of the system, i.e., the Helmholtz free energy per molecule, the internal energy per molecule, the entropy per molecule and the specific heat capacity. Second, for $T = 20$–10000 K — the classical second virial coefficient $B_{cl}$, the Boyle temperature $T_B$ and the inversion temperature $T_i$ are determined. The first quantum correction $B_{q1}$ is calculated over the temperature range $T = 20$–100 K. It turns out that it is necessary to make such a quantum correction to $B_{cl}$ for $T = 20$–60 K, whereas the quantum effects are relatively insignificant for $T > 60$ K. In general, our results are in very good agreement with previous theoretical and experimental results.

1. Introduction

The second virial coefficient $B$ of a real gas describes the first-order correction to the equation of state of the ideal gas [1] and it can be positive or negative. Positive values indicate overall repulsive interactions, whereas negative values indicate attractive interactions. The second virial coefficient $B$ provides a physical link between the particle interactions (microscopic properties) and thermodynamic (macroscopic) properties of the gas [2]. Further, $B$ can be used to predict the critical point of a liquid–gas transition [3].

In this paper we present calculations of $B$ for CH$_4$ vapor in the broad $T$-range 5 mK–10000 K. For “low” $T$ (to be defined below), $B$ should behave quantum-mechanically, whereas for higher $T$, $B$ should behave classically [4–6]. The quantum coefficient $B_q$ is studied starting with the Lippmann–Schwinger (LS) equation [7], which is essentially the Schrödinger equation in momentum space. The LS equation is solved by matrix inversion to give the corresponding phase shifts, which are then fed into the Beth–Uhlenbeck equation to evaluate $B_q$. On the other hand, both the classical second virial coefficient, $B_{cl}$, and its first quantum-mechanical correction, $B_{qc}$, are calculated from standard expressions [8, 9], based only on the intermolecular potential.

The main contribution of the present work, then, is the calculation, for the first time, of $B$ for CH$_4$ down to relatively low $T$ (5 mK), where no experimental data are available. In fact, to the best of our knowledge, no experimental values of high accuracy exist for methane below 150 K. The point is that, at “low” $T$, quantum effects are expected to make a significant contribution to $B$. Therefore, $B$ can be used to explore the interface between the classical and quantum regimes in the gas [10–12]. Also, $B_q$ can be considered as an indicator of the formation of small clusters [13]. Novoa and Whangbo [14] found that the methane dimer (CH$_4$)$_2$ is bound in all possible orientations of the molecule.

The abundance of CH$_4$ gas in nature exceeds 90% [15]. It is the simplest representative of the alkanes. A colorless and odorless gas, it is lighter than air. Its melting point is 90.7 K and its boiling point is 111.65 K [16]. In addition to its increasingly crucial role in modern energetics, it is important for generating electricity when burnt in a steam generator or gas turbine, and it is used in low-temperature fuel cells [16].

For CH$_4$ vapor, $B$ has been the subject of several theoretical [17–24] and experimental [25–29] studies. In general, these have followed closely the same method of computation as for inert gases via the classical cluster expansion, with the Lennard-Jones
potential [22]. A new approach for the exp-6 potential was proposed [30] and the formula was used to calculate \( B \) for CH\(_4\) over a broad \( T \)-range [30]. Recently, a method for the inverse problem has been reported, namely, obtaining relatively simple intermolecular potentials from (experimental) \( B \) [31].

This paper is organized as follows: Sect. 2 is a brief account of the formalism involved, Sect. 3 contains our results and their analysis. Finally, a short conclusion closes the paper in Sect. 4.

2. Formalism

2.1. Quantum second virial coefficient \( B_q \)

A full quantum mechanical study is performed to compute \( B_q \) over a temperature range 5 mK–20 K. The calculation of \( B_q \) is done by determining the phase shifts within the framework of the scattering theory [7]. Then, the calculated phase shifts are inserted into the Beth–Uhlenbeck formula to compute \( B_q \) [4].

At low \( T \), \( B_q \) is calculated using the Beth–Uhlenbeck formula [4–6]. This is given by

\[
B_q(T) = B_{\text{ideal}} + B_{\text{bound}} + B_{\text{phase}}. \tag{1}
\]

Here, \( B_{\text{ideal}} \) is the ideal-gas term, which is important in the low-temperature region, but goes to zero with increasing temperature. Namely,

\[
B_{\text{ideal}} = \frac{\lambda^3}{2 \delta^2} = -\frac{1}{2 \delta^2} \left( \frac{2 \pi \hbar^2}{m k_B T} \right)^{3/2} \tag{2}
\]

where \( \lambda \) is the thermal de Broglie wavelength, \( m \) being the \( CH_4 \) mass, \( k_B \) — the Boltzmann constant and \( \hbar = h/2\pi \) (\( h \) is Planck’s constant).

The bound-state contribution \( B_{\text{bound}} \) is given by

\[
B_{\text{bound}} = -2^{3/2} \lambda^3 \sum_{E_n} (e^{-\beta E_n} - 1). \tag{3}
\]

This term is very small and can be neglected [32].

The last term, \( B_{\text{phase}} \), represents the contribution of the scattering-state continuum and is given by

\[
B_{\text{phase}} = -\frac{2^{3/2} \lambda^5}{\pi^2} \int_0^\infty dk \, k \sum_{\ell=\text{even}} (2\ell + 1) \delta_\ell(k) e^{-\beta E(k)}, \tag{4}
\]

where \( \delta_\ell(k) \) is the \( \ell \)-partial phase shift which is a function of the wave number \( k \). The expression for \( B_{\text{phase}} \) is obtained as follows [33–35]:

- \( V_\ell(k, k') \), which is the Fourier–Bessel transform of \( V(r) \) and is needed in the next step, is calculated; \( k \) and \( k' \) are the incoming and outgoing relative momenta.
- The LS integral equation is solved, using a well-tested matrix-inversion technique, to evaluate \( \delta_\ell(k) \). The full technical details are given in [7]. This equation is valid for the present low-dense gas.
- By inserting the values of \( \delta_\ell(k) \) in (4), \( B_{\text{phase}} \) is finally determined.

2.2. Classical second virial coefficient \( B_{cl} \)

\( B_{cl} \) and its first quantum correction, \( B_{qc} \), are defined by [8, 9]:

\[
B_{cl}(T) = 2\pi \int_0^\infty dr \left( 1 - e^{-\beta V(r)} \right) r^2, \tag{5}
\]

\[
B_{qc}(T) = \frac{\pi \hbar^2 \beta^3}{6m} \int_0^\infty dr e^{-\beta V(r)} \left( V'(r) r \right)^2. \tag{6}
\]

Here, \( V'(r) \) is the first derivative of \( V(r) \) with respect to the magnitude of the intermolecular separation \( r \). The temperature parameter is defined as \( \beta = 1/(k_B T) \), and \( e^{-\beta V(r)} \) is the classical pair correlation function [36]. Note that \( B_{qc} \) is important in the “low”-\( T \) regime.

In this study, the “natural” system of units is adopted, i.e., \( h = m = k_B = 1 \). The conversion factor \( \frac{\pi^2}{m} \) for \( CH_4 \) is 3.02386638 K Å\(^2\).

2.3. \( CH_4–CH_4 \) potential

This is our main input, the assumption being that \( CH_4 \) molecules are rigid and spherical. The pseudospherical nature of methane suggests that this approximation is not unreasonable [37]. Thus, the methane interaction has been modeled as isotropic [37]; specifically, it is described by the Morse potential [38]:

\[
V(r) = D \left( e^{-2\alpha(r-r_0)} - 2 e^{-\alpha(r-r_0)} \right), \tag{7}
\]

where \( D = 149.1 \) K, \( \alpha = 1.166 \) Å\(^{-1}\) and \( r_0 = 4.50 \) Å. This is shown in Fig. 1.

3. Results and discussion

3.1. Quantum second virial coefficient \( B_q \)

At low enough \( T \), \( \lambda \) becomes comparable to the mean intermolecular distance \( \langle r \rangle \). This means that quantum-mechanical effects will dominate and the classical framework will no longer be valid. Now, \( B_q \) has its role to play.

Fig. 1. The \( CH_4–CH_4 \) potential \( V(r) \) [K] as a function of the intermolecular separation \( r \) [Å].
The quantum second virial coefficient \( B_q \) [cm\(^3\)/mol] at different temperatures \( T \) [K]. For each \( T \), the ratio of the two terms \( B_{\text{phase}} \) (5) and \( B_{\text{ideal}} \) (3) is given.

| \( T \) [K] | \( B_q \) [cm\(^3\)/mol] | \( B_{\text{phase}}/B_{\text{ideal}} \) |
|------------|-----------------|------------------|
| 5 \( \times 10^{-3} \) | \( 1.632 \times 10^4 \) | 1.66 |
| 0.01       | \( 1.220 \times 10^4 \) | 2.38 |
| 0.02       | \( 7.582 \times 10^3 \) | 3.43 |
| 0.03       | \( 5.087 \times 10^3 \) | 4.00 |
| 0.04       | \( 3.617 \times 10^3 \) | 4.28 |
| 0.05       | \( 2.754 \times 10^3 \) | 4.49 |
| 0.1        | \( 1.497 \times 10^3 \) | 6.37 |
| 0.2        | \( 1.032 \times 10^3 \) | 11.5 |
| 0.3        | \( 7.900 \times 10^2 \) | 15.7 |
| 0.4        | \( 6.242 \times 10^2 \) | 18.9 |
| 0.5        | \( 4.957 \times 10^2 \) | 20.9 |
| 1          | \( 1.281 \times 10^2 \) | 15.5 |
| 2          | –51.94 | 15.7 |
| 3          | –57.88 | 33.1 |
| 4          | –43.57 | 38.5 |
| 5          | –31.07 | 38.4 |
| 10         | –7.022 | 24.2 |
| 15         | –2.003 | 12.2 |
| 20         | –3.481 \( \times 10^{-1} \) | 2.53 |

The classical second virial coefficient \( B_{\text{cl}} \) [cm\(^3\)/mol] and its first quantum correction \( B_{\text{qc}} \) [cm\(^3\)/mol], at different low temperatures \( T \) [K].

| \( T \) [K] | \( B_{\text{cl}} \) [cm\(^3\)/mol] | \( B_{\text{qc}} \) [cm\(^3\)/mol] |
|------------|------------------|------------------|
| 20         | –8.476 \( \times 10^4 \) | 1.095 \( \times 10^4 \) |
| 25         | –2.222 \( \times 10^4 \) | 1.747 \( \times 10^3 \) |
| 30         | –9.307 \( \times 10^3 \) | 4.869 \( \times 10^2 \) |
| 35         | –5.046 \( \times 10^3 \) | 1.880 \( \times 10^2 \) |
| 40         | –3.195 \( \times 10^3 \) | 89.48 |
| 45         | –2.234 \( \times 10^3 \) | 49.11 |
| 50         | –1.671 \( \times 10^3 \) | 29.85 |
| 60         | –1.066 \( \times 10^3 \) | 13.61 |
| 70         | –7.578 \( \times 10^2 \) | 7.486 |
| 80         | –5.760 \( \times 10^2 \) | 4.652 |
| 90         | –4.576 \( \times 10^2 \) | 3.148 |
| 100        | –3.751 \( \times 10^2 \) | 2.267 |

The behavior of \( B_q \) (see Fig. 2) is similar to that of the CH\(_4\)-CH\(_4\) potential (see Fig. 1). The value of \( B_q \) is positive for \( T < 1.45 \) K. This means that the binary interaction is repulsive in this \( T\)-regime. By increasing \( T \), \( B_q \) decreases. At a particular \( T \), \( B_q \) passes through zero at the so-called “unusual” Boyle temperature (\( T_B \approx 1.45 \) K) [12], and then becomes negative. With increasing \( T \), \( B_q \) becomes more negative. It reaches a minimum, which represents the equilibrium point, at \( T = 2.54 \) K. The minimum value of \( B_q \) is \( B_{\text{min}} = –61.11 \) cm\(^3\)/mol. For \( T > 2.5 \) K, \( B_q \) becomes less negative with increasing \( T \) and it approaches zero in the higher limit of this \( T\)-range.

As neither experimental nor theoretical results are available in this \( T\)-range (5 mK–20 K), it is not possible to assess the accuracy of our results. However, the present framework has been successfully applied to a host of inert and other gases [11–13, 34, 35].

3.2. Classical second virial coefficient \( B_{\text{cl}} \) with first quantum correction \( B_{\text{qc}} \)

These have been calculated for the \( T\)-range (20–100 K), using (6) and (7). The results are presented in Table II. One can see that \( B_{\text{cl}} \) is negative over this entire range due to the presence of long-range attractive forces [39]. The contribution of short-range repulsive forces increases as \( T \) increases, causing \( B \) to become less negative. It is clear that \( B_{\text{qc}} \) is strongly temperature-dependent at low \( T \). The results indicate that \( B_{\text{qc}} \) rapidly increases as \( T \) decreases. At \( T \leq 60 \) K, it is clear that \( B_{\text{qc}} \) plays a significant role and cannot be neglected. At \( T > 60 \) K, \( B_{\text{qc}} \) is negligible because the quantum effects are small.

The classical second virial coefficient \( B_{\text{cl}} \) can be fitted as a function of \( T \). Its form is given as

\[
B_{\text{Fit}} = a + bT + c \exp \left( -\frac{d}{T^2} \right),
\]

where the fitting parameters in the regime of \( T = 100–10000 \) K are: \( a = –829.241 \) cm\(^3\)/mol, \( b = –0.0015258 \) cm\(^3\)/mol K, \( c = –1324.4 \) cm\(^3\)/K mol, \( d = 870.593 \) cm\(^3\)/mol and \( e = 3789.03 \) K\(^2\).

Figure 3 shows \( B_{\text{cl}} \) and its fitting equation, \( B_{\text{Fit}} \), in the \( T\)-range 100–10000 K. Clearly, the proposed fitting function accurately represents the behavior

Fig. 2. The dependence of the quantum second virial coefficient \( B_q \) [cm\(^3\)/mol] on the temperature \( T \) [K] (for \( T = 1–20 \) K).
of $B_{cl}$ which is very negative at “low” $T$. By increasing $T$, $B_{cl}$ becomes less negative and equals zero at the Boyle temperature ($T_B \approx 500.1$ K), where the attractive and repulsive forces are balanced. This result is in agreement with previous results [22, 40] of 507.22 K and 506 K, respectively. For $T > T_B$, $B_{cl}$ becomes positive. It continues to increase with increasing $T$, until it passes through a maximum at a certain intermediate $T$, which is called the inversion temperature ($T_i \approx 2614$ K). The maximum ($B_{cl}$)$_{\text{max}}$ occurs at $T_i \approx 2614$ K, which is associated with the Joule free expansion [41]. For $T > T_i$, $B_{cl}$ decreases and decays towards zero at very high $T$.

The accuracy of the present results can be tested by comparing our $B_{cl}$ and $T_B$ to previous theoretical [17, 18, 22, 23] and experimental [25] results, as shown in Table III. It is found that the agreement is quite good. In each case, $T_B$ is around 500 K. It is concluded that the Morse potential is quite successful in this context. For $B_{cl}$, the agreement is also good with Hellmann et al. [18], who used an intermolecular potential energy surface (PES) in their ab initio calculations, and with Somuncua et al. [17] who used the Kihara potential.

The average absolute relative deviation (AARD) for $B_{cl}$ at different $T$ has also been calculated for experimental data [25] as well as for theoretical calculations with the following potentials: (i) Morse (present); (ii) Kihara [17]; (iii) Lennard-Jones (LJ) of types 12-6 [22] and 21-6 [23]; and (iii) PES [18]. The AARD is given by

$$\text{AARD} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{B_{\text{exp}} - B_{\text{cal}}}{B_{\text{exp}}} \right| \times 100, \quad (9)$$

where $N$, $B_{\text{cal}}$ and $B_{\text{exp}}$ are, respectively, the number of data, the calculated $B$ and the experimental $B$. These AARD calculations are shown in Table IV. It is noted that the AARD for the present results is the lowest. This means that the present model surpasses the others.

### 3.3. Thermodynamic properties

Having obtained $B$, one can readily determine the pressure $P$, compressibility factor $Z$, internal energy $U$, the Helmholtz free energy $F$, entropy $S$ and specific heat capacity $C_v$ as follows [1, 42, 43]:

$$\frac{P}{nk_BT} = 1 + nB, \quad (10)$$

$$Z = 1 + nB, \quad (11)$$

$$U(T) \approx N \left[ \frac{3}{2} k_B T - nk_B T^2 \frac{dB(T)}{dT} \right], \quad (12)$$

$$F = Nk_BT \ln \left( n \lambda^3 \right) - 1 + nB(T), \quad (13)$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_V, \quad (14)$$

$$C_v = \left( \frac{dU}{dT} \right)_V. \quad (15)$$

The results have been calculated for the number density $n = 1 \times 10^{-4}$ Å$^{-3}$ and the $T$-range 1–20 K, using $B_q$. These results are displayed in Figs. 4 and 5.

![Fig. 4. (a) The pressure $P$ [Pa] as a function of the temperature $T$ [K]. (b) The compressibility factor $Z$ as a function of $T$ [K].](image)

![Fig. 5. Further thermodynamic properties of CH$_4$ as a function of the temperature $T$ [K]: (a) the Helmholtz free energy per molecule, $F/N$ [K], (b) the internal energy per molecule, $U/N$ [K], (c) the entropy per molecule, $S/k_B N$, (d) the specific heat capacity $C_v/k_B N$.](image)
Comparison of our results for the classical second virial coefficient \( B_{cl} [\text{cm}^3/\text{mol}] \) with previous results.

| \( T [\text{K}] \) | \( B_{cl} [\text{cm}^3/\text{mol}] \) | Present results | Theor. [17] | Theor. [18] | Theor. [22] | Theor. [23] | Exp. [25] |
|-----------------|---------------------------------|----------------|-------------|-------------|-------------|-------------|-----------|
| 105             | -342.7                          | -369.32        | -           | -           | -           | -           | -         |
| 110             | -314.6                          | -336.59        | -           | -334.0      | -           | -           | -         |
| 120             | -268.4                          | -283.90        | -           | -281.1      | -           | -           | -         |
| 130             | -232.2                          | -243.44        | -           | -240.7      | -           | -           | -         |
| 140             | -203.0                          | -211.46        | -           | -208.8      | -           | -           | -         |
| 160             | -159.0                          | -164.25        | -           | -161.9      | -           | -           | -         |
| 180             | -127.5                          | -131.16        | -           | -129.2      | -           | -           | -         |
| 200             | -104.0                          | -105.905       | -106.74     | -105.1      | -           | -           | -         |
| 250             | -65.00                          | -66.94         | -           | -65.8       | -           | -           | -         |
| 273.15          | -52.75                          | -54.56         | -           | -53.6       | -           | -           | -         |
| 293.15          | -44.03                          | -45.79         | -45.25      | -           | -44.95      | -           | -         |
| 298.15          | -42.08                          | -43.82         | -           | -           | -           | -           | -         |
| 300             | -41.37                          | -42.0994       | -43.11      | -42.3       | -           | -           | -         |
| 400             | -14.51                          | -15.4109       | -16.19      | -15.75      | -15.7       | -15.09      | -         |
| 450             | -6.256                          | -7.92          | -           | -7.4        | -           | -           | -         |
| 490             | -1.079                          | -2.72          | -           | -           | -           | -           | -         |
| 500             | 6.167 \times 10^{-2}            | -1.01061       | -1.57       | -0.82       | -1.1        | 0.39        | -         |
| 510             | 1.149                           | 0.48           | -           | -           | -           | -           | -         |
| 550             | 5.027                           | 3.43           | -           | 4.0         | -           | -           | -         |
| 600             | 9.010                           | 7.92903        | 7.47        | 8.55        | 8.1         | 10.43       | -         |
| 650             | 12.26                           | 10.78          | -           | 11.5        | -           | -           | -         |
| 700             | 14.95                           | 13.967         | 13.53       | 14.91       | 14.3        | 17.51       | -         |
| 800             | 19.11                           | 18.2851        | 17.83       | 19.46       | 18.8        | 22.77       | -         |
| 900             | 22.12                           | 21.5034        | 21.00       | 22.84       | 22.1        | 26.83       | -         |
| 1000            | 24.37                           | 23.978         | 23.41       | 25.42       | 24.7        | 30.07       | -         |
| 1200            | 27.42                           | 26.75          | 29.06       | 29.8        | 34.92       | -           | -         |
| 1400            | 29.28                           | -              | 31.44       | -           | 38.37       | -           | -         |
| 1600            | 30.44                           | -              | 33.05       | -           | 40.95       | -           | -         |
| 1800            | 31.18                           | -              | 34.19       | -           | 42.96       | -           | -         |
| 2000            | 31.64                           | -              | 35.00       | -           | 44.56       | -           | -         |
| 2400            | 32.04                           | -              | 36.02       | -           | 46.97       | -           | -         |

Comparison of the average absolute relative deviation (AARD) in the calculation of \( B_{cl} \), using (i) the Morse potential (present results), (ii) Kihara [17], (iii) Lennard-Jones (LJ) of types (12-6) [22] and 21-6 [23]) and (iii) intermolecular potential energy surface (PES) [18].

| \( N \) | \( T \)-range [K] | Present results | Theor. [17] | Theor. [18] | Theor. [22] | Theor. [23] |
|---------|------------------|----------------|-------------|-------------|-------------|-------------|
| 14      | 293.15-2400      | 293.15-2400    | 293.15-1200 | 293.15-2400 | 293.15-1200 |             |
| 7       | 293.15-2400      | 293.15-2400    | 293.15-2400 | 293.15-2400 | 293.15-2400 |             |
| 9       | 293.15-1200      | 293.15-1200    | 293.15-2400 | 293.15-2400 | 293.15-2400 |             |
| 14      | 293.15-2400      | 293.15-2400    | 293.15-2400 | 293.15-2400 | 293.15-2400 |             |

The \( P-T \) curve is shown in Fig. 4a. It is observed that \( P \) rises monotonically with increasing \( T \), and it is almost linear in this region of \( T \). Figure 4b displays the \( Z-T \) curve. At very low \( T \) (\( \leq 5 \text{ K} \)), \( Z \) is strongly-dependent on \( T \); “nonideality” occurs. Further, \( Z \) decreases rapidly with increasing \( T \) and it reaches a minimum at about \( T \approx 2.54 \text{ K} \). For \( T > 5 \text{ K} \), \( Z \) decreases less rapidly and approaches 1 at \( T = 15-20 \text{ K} \). The same occurs at \( T_B \approx 1.45 \text{ K} \), with \( B_{cl} \to 0 \). There, the system behaves as an ideal gas. Generally, the behavior of \( Z \) as a function of \( T \) is rather the same as the behavior of \( B_{cl} \).
Figure 5a displays $F$ as a function of $T$. One can observe that $F$ decreases linearly with increasing $T$. In contrast, $U$ (see Fig. 5b) increases as $T$ increases (with the kinetic energy increasing) and exhibits a linear dependence on $T$. Figure 5c indicates a substantive increase of $S$ as $T$ increases. Finally, $C_v$ is plotted as a function of $T$ in Fig. 5d. It is nearly independent of $T$, since $\frac{C_v}{k_B} \approx 1.5$.

4. Conclusion

The subject of this work was the second virial coefficient $B$ of CH$_4$ vapor in the broad temperature range (5 mK–10000 K). Specifically, $B$ was computed in two temperature regions:

1. Temperature region $T \leq 5$ mK–20 K: the quantum second virial coefficient $B_q$ was calculated. This is the first time that $B_q$ for CH$_4$ has been studied. It was found that $B_q$ behaves with $T$ in much the same way as the behavior of the intermolecular CH$_4$–CH$_4$ potential with the intermolecular separation $r$;

2. Temperature region $T = 20 – 10000$ K: the classical second virial coefficient $B_{cl}$, the Boyle temperature $T_B$ and the inversion temperature $T_i$ were determined. Therefore, it was the first quantum correction $B_{qcl}$ for the $T$-region (20–100 K). It was found that it is necessary to make quantum corrections to the $B_{cl}$ for $T = 20–60$ K, whereas the quantum effects for $T > 60$ K are relatively insignificant. In general, our results for $B_{cl}$ are in good agreement with previous theoretical and experimental results.

Then, $B_q$ was used to investigate the (pressure $P$–number density $n$–$T$) behavior of CH$_4$ vapor, as well as other its thermodynamic properties: the Helmholtz free energy $F$, internal energy $U$, entropy $S$, compressibility factor $Z$ and specific heat capacity $C_v$ in the $T$-region (1–20 K) for $n = 1 \times 10^{-3}$ Å$^{-3}$.

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