Modified 2CLJDQP model and the second virial coefficients for linear molecules*

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A modified form of 2CLJDQP potential model is proposed to calculate the second virial coefficients of two-center Lennard-Jones molecules. In the presented potential model, the potential parameters σ and ε are considered as the temperature-dependent parameters in the form of hyperbolical temperature function based on the theory of temperature-dependent potential parameters. With this modified model, the second virial coefficients of some homonuclear molecules (such as O_2, Cl_2, CH_3CH_3, and CF_3CF_3) and heteronuclear molecules (such as CO, NO, CH_3F, CH_3Cl, CH_3CF_3, CH_3CHF_2, and CF_3CH_2F) are calculated. Then the Lorentz–Berthelot mixing rule is modified with a temperature-dependent expression, and the second virial coefficients of the heteronuclear molecules (such as CH_3F, CH_3Cl, and CH_3CF_3) are calculated. Moreover, CO_2 and N_2O are also studied with the modified 3CLJDQP model. The calculated results from the modified 2CLJDQP model accord better with the experimental data than those from the original model. It is shown that the presented model improves the positive deviation in low temperature range and negative deviation in high temperature range. So the modified 2CLJDQP potential model with the temperature-dependent parameters can be employed satisfactorily in large temperature range.

Keywords: potential function, temperature-dependent parameters, linear molecules, second virial coefficients

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1. Introduction

The key to understanding the nature of matter is to investigate the structure and interaction of molecules, so it is necessary to develop potential models that are accurate enough to indicate the features of matter and simple enough to employ.[1] The studies of intermolecular potential have developed enormously in the past forty years. The researchers have provided us with an insight into the basic physical problems, and a large number of relevant industrial applications have been found. Potential function has been known as the basis of gas kinetic theory, liquid perturbation function, and distribution function.[2,3] Generally, the pair potential function with satisfactory accuracy has been employed to determine the transport (viscosity, diffusion, etc.) and thermodynamic (sound speed, virial coefficients, etc.) properties of fluids.[4,5] Recently, some researchers have introduced the potential function to investigate the fourth order virial equation of state and to estimate the elastic characteristics of bulk solids.[6–8] In addition, it is crucial for molecular simulation to choose a proper potential function.

The well-known Lennard-Jones (LJ) potential function which is the defacto standard in molecular simulation was proposed in 1924.[9] It is particularly accurate to investigate the properties of monatomic molecules, but it is not suitable for the spherically unsymmetrical polar molecules. Later, the two-center Lennard-Jones model (2CLJ) and its derivatives such as 2CLJD, 2CLJQ, etc. were developed.[10–14] and were used to study the common linear molecules such as N_2, O_2, Cl_2, F_2, CO, CO_2, NO, C_2H_6, C_2F_6, CH_3F, etc.[15–22] The 2CLJDQP model derived from 2CLJD and 2CLJQ was presented by Meng and Duan in 2006.[23] in which the dipole, quadrupole, and induction effects as well as the rotation of the dipole out of molecular axis were introduced to describe the intermolecular forces more truly. However, like other LJ-type potential functions, this model is probably not suited for calculating the second virial coefficients in a large temperature range. The calculation results indicated that the negative deviation at high temperature and positive deviation at low temperature would arise.[23] Maybe there are two reasons: firstly, the virial expansion theory is not applicable for dense gases nor liquids at low temperature, although it may obtain good results at the expense of calculation accuracy in high temperature range; secondly, it is not proper to treat the potential parameters as constants in large temperature range, which has been presented in some studies.[24] The novel point of this work is to propose a modified 2CLJDQP potential function by introducing the temperature-dependent parameters.

The rest of this paper is organized as follows. In Section 2, the temperature-dependent potential parameters are introduced into the 2CLJDQP potential function to improve the model applicability in large temperature range and the modified 2CLJDQP potential function is proposed. In Section 3,

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the second virial coefficients are selected as the criterion to verify the present model, and the calculation of the potential parameters of the modified 2CLJDQP are given. In Section 4, by coupling the modified 2CLJDQP potential function with the Lorentz–Berthelot mixing rule, the second virial coefficients of Cl_2, C_2H_6, C_2F_6, CO, CH_3Cl, CH_3CF_3, CH_3CH_2F, CH_3CHF_2 are calculated in the high and low temperature ranges. Moreover, the second virial coefficients of CO_2 and N_2O are also calculated using the modified 3CLJDQP potential in this section. Some results obtained in this work are discussed in Section 5, and finally some conclusions are drawn from the present study in Section 6.

2. Potential model

The 2CLJ potential function was proposed by Sweet and Steele (1967),[25] which is the primary model for simple linear molecules. Kong (1970)[26] and Murthy (1981)[27] introduced the dipole and quadrupole to the mass center and improved this model, which were named 2CLJD and 2CLJQ, respectively. Santisa and Frattinia (1987)[28] proposed the dipole effect in 2CLJQ model. Recently, Meng and Duan[23] presented the molecular polarizability by introducing two polarization angles to make the long-range interactions more realistic. This model is referred to as 2CLJDQP:[23,29]

$$u_{\mathrm{2CLJDQP}} = \sum_{i=1}^{2}\sum_{j=1}^{2} u_{ij}^{\mathrm{LJ}} + u_{\mathrm{ele}} + u_{\mathrm{ind}}, \tag{1}$$

where

$$u_{ij}^{\mathrm{LJ}}(r) = 4\varepsilon_{ij}\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}\right], \tag{2}$$

$$u_{\mathrm{ele}} = u(\mu,\mu) + u(\mu,Q) + u(Q,Q), \tag{3}$$

$$u_{\mathrm{ind}} = u(\mu,\mathrm{ind}\,\mu) + u(\mu Q,\mathrm{ind}\,\mu) + u(Q,\mathrm{ind}\,\mu), \tag{4}$$

μ, Q, and ind μ are permanent dipole, permanent quadrupole, and induced dipole, respectively. The calculations of the dominant electrostatic and induced interactions can be found in many classical statistical textbooks as well as in the literature.[23,30]

As the potential function mentioned above, more and more forces were put forward, such as octopole, hexadecapole, and higher dispersion contributions.[26–28,31–33] However, another perspective on developing potential function was considered to introduce the temperature-dependent potential parameters.[8,34–36]

Normally, gas can be considered as the molecular mixture of different excited states at different temperatures.[37] The vibrational partition function of one molecule is

$$Z = 1 + \sum_{n=1}^{\infty}\sum_{\upsilon_1=0}^{n}\cdots\sum_{\upsilon_N=0}^{n-\upsilon_1-\cdots-\upsilon_{N-1}}\prod_{i=1}^{N} g_{\upsilon i}\exp(-\upsilon_i\theta_i/T), \tag{5}$$

where N is the total number of normal vibrations, υ_i is the number of the vibrationally excited level of the i-th normal vibration, $g_{\upsilon i}$ is the degeneracy and $\theta_i = h\nu_i/k$, and ν_i is the i-th normal frequency. For light molecules, the vibrational frequencies are high and at normal temperatures almost all molecules are in the ground state. Therefore we can expect that a unique intermolecular interaction would be a fair approximation to the problem of calculating thermodynamic properties. In contrast, for molecules with heavier atoms, even small differences among all these different potentials would lead to substantial changes in the overall interaction with temperature changing, because according to the mixture rule

$$B = \sum_{k,l} x_k x_l B_{kl}, \tag{6}$$

where x_k and x_l are the relative populations of levels (including the ground state) and B_{kl} is the second virial coefficient calculated by the corresponding potential functions $u(k,l)$; k and $l = 0$ or υ_i and $\upsilon_j = 0$. Based on the enlargement of the size of the vibrationally excited states, the mixture of all differently enlarged states at a given temperature is considered as an average state. Thus the pair interactions can be described by a single effective potential with characteristic distance and potential well-depth dependent on the temperature.

The characteristic distance between molecules increases slightly with the increase of temperature, while the potential well-depth decreases with temperature increasing, and the temperature effect is more intense for heavy molecules.[28] The temperature-dependent potential can be obtained from Boltzmann averaging of the intermolecular potential over different quantum states.[34,35,38] Hohm and Zarkova[39] presented a Lennard-Jones (n-6) temperature- dependent potential (LJTDP), which is very suitable for globular molecules and can be extended to simple linear molecules.[40,41] Then some different temperature-dependent functions such as linear,[42] double-exponential,[27] hyperbolic,[36] etc. were proposed.

When the 2CLJDQP model is used to calculate the second virial coefficients, the obvious deviations between calculated results and experimental data can be found. Typically, the results indicate that the calculated second virial coefficients are extraordinarily larger than experimental data at low temperature and slightly smaller than experimental data at high temperature. To modify the 2CLJDQP potential function at low temperature more intensively, we choose the hyperbolical temperature function for characteristic distance correction. As shown in Eq. (8), the characteristic distance changes more steeply with temperature changing in low temperature range than in high temperature range. If the reasonable assumption that the long-ranged dispersion energy does not depend on the temperature holds, the power function for potential well-depth can be corrected into Eq. (9).[42] In this case, the 2CLJDQP model is modified by

$$u_{ij}^{\mathrm{LJ}}(r,T) = 4\varepsilon_{ij}(T)\left[(\sigma(T)/r_{ij})^{12} - (\sigma(T)/r_{ij})^{6}\right], \tag{7}$$

$$\sigma(T) = \sigma^{\infty} - \delta/T, \tag{8}$$

$$\varepsilon(T) = \varepsilon^{\infty} \cdot (\sigma^{\infty}/\sigma)^6, \tag{9}$$

where $\sigma(T)$ and $\varepsilon(T)$ are the effective potential parameters that result from the vibrational excitation of molecules; σ^{∞} and ε^{∞} are potential parameters when temperature is infinitely high, which can be obtained by fitting; δ is the temperature enlargement factor, which is a fitted parameter and independent of temperature. For the simple two-center molecules such as N_2, O_2, and F_2, the molecular vibration frequency is high and most of molecules are in the ground state, hence temperature affects the potential parameters slightly, then δ would approach to 0, and equation (17) would degenerate to Eq. (2).

3. Calculation of potential parameters

The potential parameters of the modified 2CLJDQP are determined by solving a typical ill-posed inverse problem of minimizing the root-mean-square deviation (RMSD) between measured and calculated thermodynamic properties (see Eq. (10)). Only the second virial coefficients are used as the criterion in this work, because it is difficult to make the calculated and measured transport properties (viscosity or diffusivity) be in good agreement with each other and the calculated and measured thermodynamic properties under the same parameters for complex molecules in a large temperature range be in accordance with each other

$$\mathrm{RMSD} = \sqrt{\sum_{i=1}^{n} \left(B_{\mathrm{exp}} - B_{\mathrm{cal}}\right)^2 / n}. \tag{10}$$

The expression deduced from molecule physics for the second virial coefficient is given by

$$\begin{aligned} B(T) &= -\frac{N_{\mathrm{A}}}{32\pi^3} \int_0^{\infty} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \left(\mathrm{e}^{-u(T)/kT} - 1\right) \\ &\quad \times r^2 \,\mathrm{d}r \,\mathrm{d}\psi_1 \,\mathrm{d}\psi_2 \sin\theta_1 \,\mathrm{d}\theta_1 \sin\theta_2 \,\mathrm{d}\theta_2 \,\mathrm{d}\varphi_1 \,\mathrm{d}\varphi_2, \end{aligned} \tag{11}$$

where N_{A} is the Avogadro constant, k is the Boltzmann constant, T is the absolute temperature, $u(T)$ is the potential between two molecules, r is the distance between the two molecular centers, ψ_1, ψ_2, θ_1, θ_2, φ_1, and φ_2 are the orientation angles of two linear molecules. The seven-fold integration is calculated with the Monte Carlo method. In order to compare with the 2CLJDQP model conveniently, 5×10^8 random samplings from the Mersenne twister are adopted.[43] This pseudorandom number generator has a very long period ($2^{19937} - 1$), which is far greater than the number of the samplings, so the calculation error caused by the pseudorandom number generator can be neglected. The samplings of r are chosen between $r = 0.3\sigma(T)$ and $r = 20\sigma(T)$. For $0 < r < 0.3\sigma(T)$, the value of potential function shown in Eq. (17) varies disastrously, which would lead to mistakes in integrating Eq. (11). In this range, it is assumed that the molecules behave like hard sphere molecules to avoid overflow of the Mayer function. For the range $r > 20\sigma(T)$, the interaction among molecules can be ignored because it is very weak. Another method for this difficult integration was proposed by Conroy[44] and improved by Nezbeda *et al.*[45] It has been verified that the results from the two methods agree very well within a deviation of less than 0.5%.[29]

It should be noted that the values of dipole, quadrupole, polarizability, and other molecular properties serving for calculating the 2CLJDQP potential can be found in Ref. [23]. In the present work, we focus on the modified part of the 2CLJDQP potential. For calculating the parameters of Eqs. (8) and (9) accurately and quickly, the potential parameters of the 2CLJDQP model are used. The calculated results of the second virial coefficients by the 2CLJDQP model may present positive deviation in low temperature range and negative deviation in high temperature range, which can be named the seesaw phenomenon figuratively. We define the optimal temperature T_{opt} as the temperature value corresponding to the intersection point between the second virial coefficient curve calculated from 2CLJDQP model and that fitted by the experimental data. We can calculate the exact value of T_{opt} by the iterative method; however, it is a time-consuming process. Usually T_{opt} is estimated from the intersection point of the two curves, and it is proved that the uncertainty due to this estimation can be ignored. Then the 2CLJDQP parameters and T_{opt} can be substituted into Eqs. (8) and (9), whose freedom degree decreases to one, and it is easy to calculate the potential parameters of the modified 2CLJDQP model from fitting. Take C_2H_6 for example. Firstly, estimating T_{opt} to be about 342 K and then substituting it into Eqs. (8) and (9), we can obtain $4.10 = \sigma^{\infty} - \delta/342$ and $93.9 = \varepsilon^{\infty}/k \cdot (\sigma^{\infty}/4.10)^6$ because of $\sigma = 4.10 \times 10^{-10}$ m and $\varepsilon/k = 93.9$ K for 2CLJDQP model as listed in Table 1. Secondly, express σ^{∞} and ε^{∞}/k as a function

Table 1. Potential parameters of 2CLJDQP and modified 2CLJDQP model for the homonuclear diatomics and C_2 derivatives.

Molecule	$(\sigma \times 10^{10})$/m Ref. [23]	(ε/k)/K Ref. [23]	B_{RMSD}/cm^3·mol^{-1}	$(\sigma^{\infty} \times 10^{10})$/m	(ε^{∞}/k)/K	$(\delta \times 10^{10})$/m·K	B_{RMSD}/cm^3·mol^{-1}
O_2	3.02	51.4	5.5	3.02	51.4	0	5.5
Cl_2	2.81	203.0	17.8	2.83	194.5	18.0	5.8
C_2H_6	4.10	93.9	5.3	4.16	86.1	20.5	4.4
C_2F_6	4.28	91.1	37.3	4.35	82.7	17.5	15.8

of $\delta[\sigma^{\infty} = 4.10 + \delta/342,\ \varepsilon^{\infty}/k = 93.9 \times 4.10^6/(4.10 + \delta/342)^6]$ and substitute them into Eq. (11) for calculating the best value of δ. Here, $\delta = 20.5$ m·K is obtained by fitting. Finally, the potential parameters $\sigma^{\infty} = 4.16 \times 10^{-10}$ m and $\varepsilon^{\infty}/k = 86.1$ K are calculated with the value of δ. In the present work, we avoid calculating the temperature enlargement from the spectral of molecules, because the original spectral data for complex molecules is hard to know.[34]

4. Energy parameters in the modified 2CLJDQP model

4.1. Homonuclear diatomics and C_2 derivatives

For the light molecules like N_2, O_2, and F_2, the potential parameters vary with temperature slightly, and the potential function with temperature modification will degenerate to 2CLJDQP model. So the heavy and complex molecules such as Cl_2 and C_2H_6 are studied. Here we follow Dymond's recommended curve in the book series titled "Virial Coefficients of Pure Gases and Mixtures", in which a great number of second virial coefficients data are listed and fitted to polynomials.

The calculations indicate that the second virial coefficients from the modified 2CLJDQP model are more accurate compared with those from the 2CLJDQP model. The optimized values of σ^{∞}, ε^{∞}/k, and δ are listed in Table 1. It is obvious that the potential parameters for O_2 are the same, and the temperature enlargement factor for O_2 is zero. The experimental second virial coefficients of Cl_2 are lacking and have large deviations among different data sources, so the consistency between calculated curve and experimental data is unsatisfactory especially in the low temperature range.

For C_2F_6 and C_2H_6, the RMSDs of the modified model are much smaller than those of 2CLJDQP model, since the temperature-dependent factors cannot be ignored. The parameters of 2CLJDQP model are just effective values in the large temperature range. The fitted parameters are listed in Table 1 and the calculated second virial coefficients are shown in Fig. 1 for Cl_2 and Fig. 2 for C_2H_6. It is shown that the value

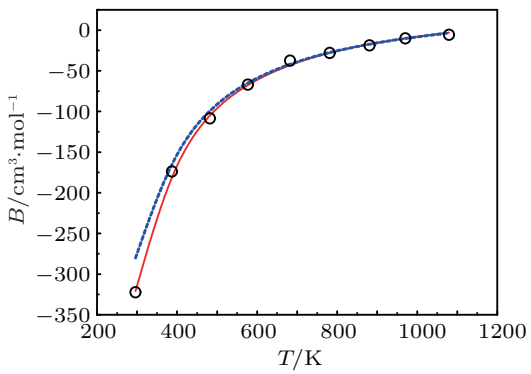


Fig. 1. (color online) Second virial coefficients of Cl_2: symbol circle for experimental data; dash line for calculated results with 2CLJDQP model; and solid line for calculated results with the modified 2CLJDQP model.

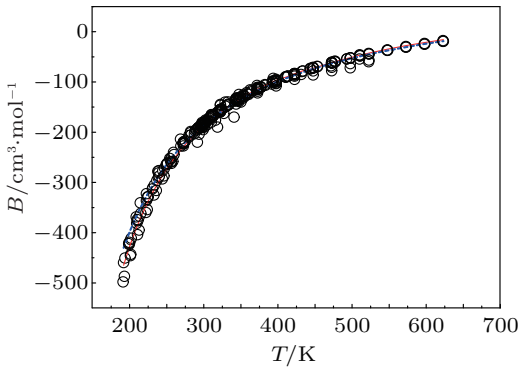


Fig. 2. (color online) Second virial coefficients of CH_3CH_3: symbol circle for experimental data; dash line for calculated results with 2CLJDQP model; and solid line for calculated results with the modified 2CLJDQP model.

of σ^{∞} in modified 2CLJDQP model is always greater than σ in 2CLJDQP, and ε^{∞}/k is less than ε/k.

4.2. Heteronuclear diatomics and their derivatives

To avoid more parameters being introduced, the homonuclear diatomics parameters are employed with Lorentz–Berthelot mixing rule for the heteromuclear diatomics like CH_3F, CH_3Cl, and CH_3CF_3. If the Lorentz–Berthelot mixing rule is used directly, it is verified that the calculated second virial coefficients have large deviations from the experimental data, because the long range attraction between two different molecular cores is much greater than that between the corresponding homonuclear molecules.[46] So the Lorentz–Berthelot mixing rule is improved on Eq. (10) and Eq. (11) for fitting the potential parameters with the expression $(\zeta_0 + \zeta_{ij}/T)$ which is similar to the constant ξ used in the 2CLJDQP potential.

The following two equations:

$$\sigma_j = 0.5(\sigma_i + \sigma_j) \tag{12}$$

and

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}[1 - (\zeta_0 + \zeta_{ij}/T)] \tag{13}$$

denote the departures from the other unknowable forces that arise in heteronuclear molecules. The constant ζ_{ij} quantifies the modification for ε with the temperature variation.

For CO, $\zeta_0 = 0$ and $\zeta_{ij} = 0$ are obtained with the parameters $\sigma_{C-C} = 3.5 \times 10^{-10}$ m and $\varepsilon_{C-C}/k = 29.1$ K, while the nonzero parameters ζ_0 and ζ_{ij} are obtained for other heteronuclear molecules. Taking CH_3Cl for example, u_{LJ}(CH_3–CH_3) and u_{LJ}(Cl–Cl) can be determined from the parameters of homonuclear molecules CH_3CH_3 and Cl_2, respectively. Since $u_{2CLJ} = u_{LJ}$(CH_3–CH_3) + $2u_{LJ}$(CH_3–Cl) + u_{LJ}(Cl–Cl), u_{LJ}(CH_3–Cl) is the key point for calculating the potential of CH_3Cl. However, the parameters of CH_3Cl cannot be determined from CH_3–CH_3 and Cl–Cl directly, because the dispersion forces and the other long-range forces between the two

heteronuclear molecules are always much greater than those between the corresponding homonuclear molecules. Therefore, the potential parameters for CH_3–Cl should be calculated with the modified Lorentz–Berthelot mixing rule, and the temperature-dependent factors can be fitted from the experimental second virial coefficients. The calculated parameters and the calculated results of second virial coefficients are shown in Table 2 and Figs. 3–6. The values of ζ_0 and ζ_{ij} are always negative, and the temperature correction is stronger with the greater absolute value ζ_{ij}.

Table 2. Potential arameters of 2CLJDQP and modified 2CLJDQP model for the heteronuclear diatomics and C_2 derivatives.

Molecule	ξ [23]	B_{RMSD}/cm^3·mol^{-1}	ζ_0	ζ_{ij}/K	B_{RMSD}/cm^3·mol^{-1}
CO	0	0.7	0	0	0.7
NO	–0.27	14.4	–0.1	–73	9.1
CH_3Cl	–0.2	9.2	–0.1	–36	8.5
CH_3F	–0.5	4.7	–0.4	–33	3.2
CH_3CF_3	–0.5	25.8	0.1	–201	6.8
CH_3CHF_2	–0.6	64.2	–0.1	–168	5.6
CF_3CH_2F	–0.85	33.4	–0.1	–248	6.3
CO_2	–0.3	1.3	–0.25	–15	0.8
N_2O	–0.95	15.6	–0.85	–38	10.7

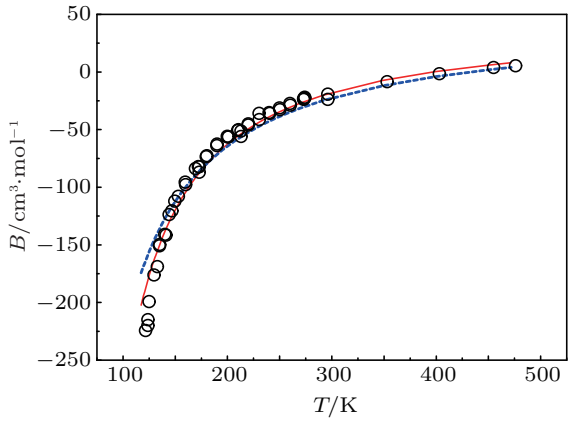


Fig. 3. (color online) Second virial coefficients of NO: circle for experimental data; dash line for calculated results with 2CLJDQP model; and solid line for calculated results with the modified 2CLJDQP model.

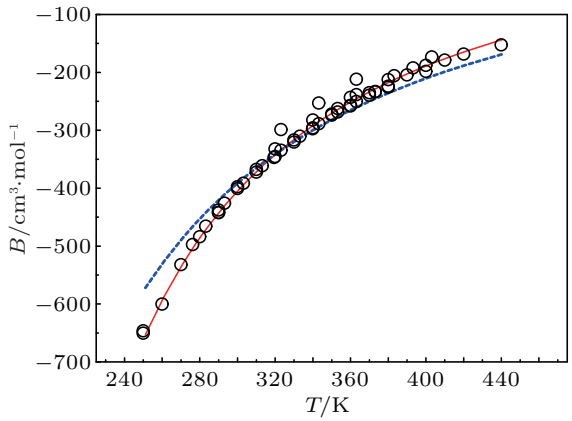


Fig. 5. (color online) Second virial coefficients of CH_3CF_3: circle for experimental data; dashed line for calculated results with 2CLJDQP model; and solid line for calculated results with the modified 2CLJDQP model.

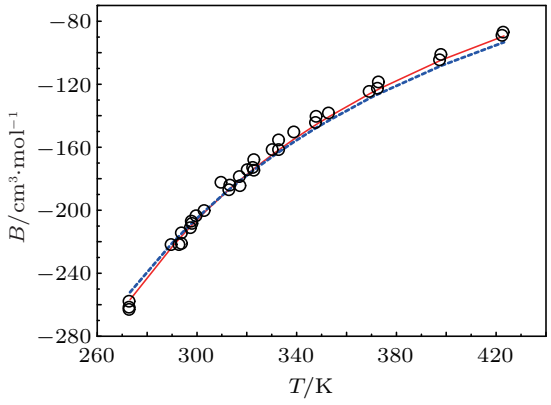


Fig. 4. (color online) Second virial coefficients of CH_3F: circle for experimental data; dashed line for calculated results with 2CLJDQP model; and solid line for calculated results with the modified 2CLJDQP model.

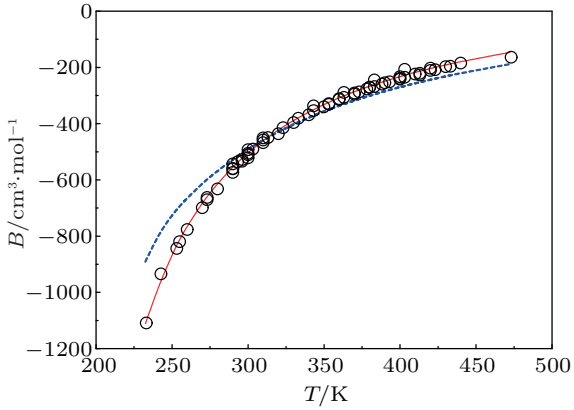


Fig. 6. (color online) Second virial coefficients of CH_3CHF_2: circle for experimental data; dashed line for calculated results with 2CLJDQP model; and solid line for calculated results with the modified 2CLJDQP model.

For CH_3CHF_2 and CF_3CH_2F, instead of calculating the potential parameters of CHF_2 and CH_2F from the second virial coefficients of the molecules CHF_2CHF_2 and CH_2FCH_2F, it is assumed that the changes of σ and ε are linear when an H is substituted by an F in CH_3. Then, the potential parameters can be obtained by interpolation, $\sigma^{\infty} = 4.22 \times 10^{-10}$ m, $\varepsilon^{\infty}/k = 84.8$ K, $\delta = 19.5 \times 10^{-10}$ m·K for CHF_2–CHF_2 and $\sigma^{\infty} = 4.29 \times 10^{-10}$ m, $\varepsilon^{\infty}/k = 83.7$ K, $\delta = 18.5 \times 10^{-10}$ m·K

for CH_2F–CH_2F. The other CH_3–CHF_2 and CF_3–CH_2F of heteronuclear interaction can be obtained from the Lorentz–Berthelot mixing rule. The results show that the calculated results are in much better agreement with the experiment data than the results from the 2CLJDQP model. The fitted parameters are listed in Table 2 and the calculated second virial coefficients curves are shown in Fig. 6 for CH_3CHF_2 and Fig. 7 for CF_3CH_2F.

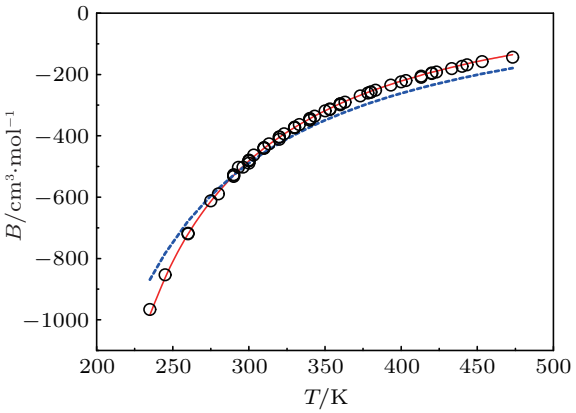


Fig. 7. (color online) Second virial coefficients of CF_3CH_2F: circle for experimental data; dashed line for calculated results with 2CLJDQP model; and solid line for calculated results with the modified 2CLJDQP model.

4.3. Triatomic linear molecules

For CO_2 and N_2O, the three-center Lennard-Jones (3CLJ) potential is proposed naturally.[27] To reduce the calculated deviation of second virial coefficients at low temperature, the modified 3CLJDQP model is also studied in this work for linear triatomic molecule, which has nine site–site interactions. Like the modified 2CLJDQP model, the heteronuclear site–site interaction is calculated by the modified Lorentz–Berthelot mixing rule. The fitted parameters for CO_2 and N_2O are given in Table 2 and the calculated second virial coefficients are shown in Fig. 8 for CO_2 and those for N_2O are displayed in Fig. 9. The temperature influence parameter for CO_2 is $\zeta_{ij} = -15$, which is closer to zero than that for N_2O. In other words, the temperature correction of 3CLJDQP for CO_2 is less than that for N_2O, which can also be seen in Figs. 8 and 9. The

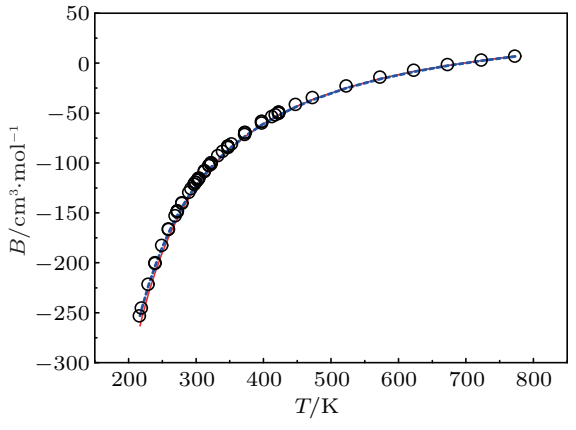


Fig. 8. (color online) Second virial coefficients of CO_2: circle for experimental data; dashed line for calculated results with 2CLJDQP model; and solid line for calculated results with the modified 2CLJDQP model.

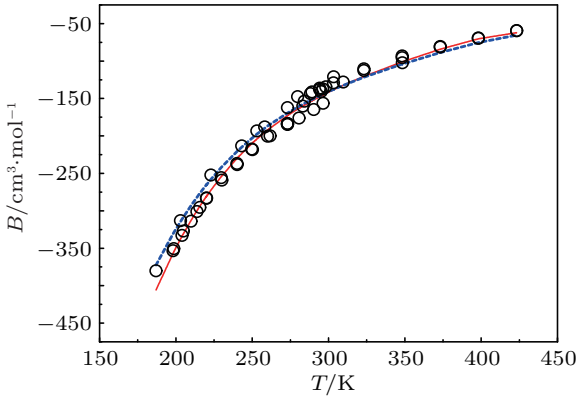


Fig. 9. (color online) Second virial coefficients of N_2O: circle for experimental data; dashed line for calculated results with 2CLJDQP model; and solid line for calculated results with the modified 2CLJDQP model.

calculated second virial coefficients curve of CO_2 with modified 3CLJDQP are close to that with 3CLJDQP model, while for N_2O the two curves deviate from each other greatly at low temperature. In addition, it is found that the absolute value of ξ in the 2CLJDQP model and ξ_0 in the modified 2CLJDQP model for N_2O are both much larger than those for CO_2, which maybe results from the difference in molecule structure between CO_2 and N_2O. The structure of N_2O (N≡N=O) is not as symmetrical as that of CO_2 (O=C=O), so the correction for N_2O is larger than that for CO_2. Further investigation about this difference is necessary.

5. Discussion

The 2CLJDQP potential has already considered the interaction between dipole moment and quadrupole moment, which is accurate enough to calculate the second virial coefficients of homonuclear and heteronuclear molecules in the moderate and high temperature ranges. However, when the long-range forces arise intensively for the heavy molecules in low temperature range, the potential parameter variation which depends on temperature cannot be neglected. The purpose of this work is to introduce the temperature-dependent potential parameters from the LJTDP model in order to modify the 2CLJDQP model and calculate the second virial coefficients. As predicted by the theory, the results shown in Table 1 indicate that the characteristic distance σ at the infinite temperature is larger than the effective σ in the 2CLJDQP model while it is contrary to the well depth ε. The positive temperature enlargement factor δ indicates that σ increases with the increase of temperature while the ε decreases with the increase of temperature. In this paper, the hyperbolic function is used for temperature correction of σ and power-dependent function is used for correction of ε. Therefore, the larger correction can be induced in the low temperature range, while slight correction in the high temperature range. For the heteronuclear molecules, the temperature-dependent factor is introduced to modify the Lorentz–Berthelot mixing rule, and the seesaw phenomenon can be greatly weakened.

In addition, the second virial coefficients of CF_3CH_2F as an example from 2CLJDQP and modified 2CLJDQP potential

are compared with those from the semi-empirical correlations. Tsonopoulos[47,48] gave a widely used expression for second virial coefficients as

$$B_r = \frac{BP_c}{RT_c} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + f^{(2)}(T_r), \tag{14}$$

where

$$f^{(0)} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8}, \tag{15}$$

$$f^{(1)} = 0.0637 - \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8}, \tag{16}$$

$$f^{(2)} = \frac{a}{T_r^6}. \tag{17}$$

In Eq. (14), T_c and P_c are the critical temperature and pressure, $R = 8.314472\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ is the universal gas constant, ω is the acentric factor, and a is related to the reduced dipole moment μ_r. For the halogenated methanes and ethanes, Tsonopoulos proposed the correlation a as

$$a_{\mathrm{Tsonopoulos}} = -2.188 \times 10^{-11}\mu_r^4 - 7.831 \times 10^{-21}\mu_r^8. \tag{18}$$

Weber[49] omitted the last term of Eq. (16) and proposed the correlation a as

$$a_{\mathrm{Weber}} = -9 \times 10^{-7}\mu_r^2. \tag{19}$$

In 2004, Meng *et al.*[50] fitted the new experiment data of second virial coefficients and redefined Eqs. (15) and (16) as

$$f^{(0)} = 0.13356 - \frac{0.30252}{T_r} - \frac{0.15668}{T_r^2} - \frac{0.00724}{T_r^3} - \frac{0.00022}{T_r^8}, \tag{20}$$

$$f^{(1)} = 0.17404 - \frac{0.15581}{T_r} + \frac{0.38183}{T_r^2} - \frac{0.44044}{T_r^3} - \frac{0.00541}{T_r^8}, \tag{21}$$

$$a_{\mathrm{Meng}} = -1.1524 \times 10^{-6}\mu_r^2 + 7.2238 \times 10^{-11}\mu_r^4 - 1.8701 \times 10^{-15}\mu_r^6. \tag{22}$$

For CF_3CH_2F, $T_c = 374.25$ K, $P_c = 4.059$ MPa.[49] $\omega = 0.326$,[5] and $\mu_r = 121.17$.[50] The deviations between the calculated second virial coefficients and experimental data are shown in Fig. 10. Normally the experimental data are scattered, and we use the mean value if several different values are proposed at the same temperature. It is obvious that the results from the modified 2CLJDQP potential are in good agreement with the results from the Meng's correlation and better than those from the Tsonopoulos's correlation and Weber's correlation at moderate temperature. While at high temperature, the results from the modified 2CLJDQP have positive errors and the semi-empirical correlations have a better accuracy.

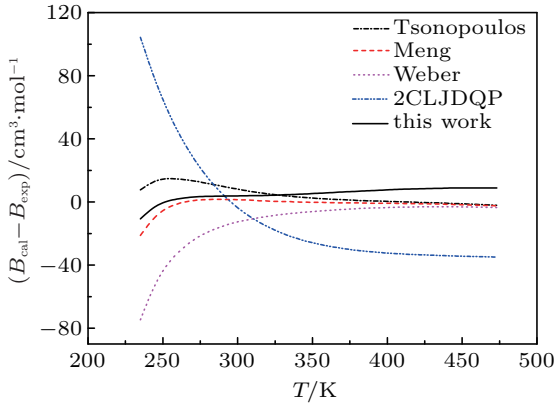


Fig. 10. (color online) Deviations of calculated second virial coefficients of CF_3CH_2F from experimental data.

In this work, all the temperature-dependent factors are obtained from purely fitting the second virial coefficients, and further studies should be extended to the calculating of the temperature correction factor from the data of molecular spectrum in a statistical physics way.

6. Conclusions

It is found that the calculated second virial coefficients from 2CLJDQP model are larger than the experimental data at low temperature and smaller than the experimental data at high temperature. To improve the so-called seesaw phenomenon in calculation of second virial coefficients, the temperature-dependent modification of 2CLJDQP potential is proposed based on the theory of Lennard-Jones temperature-dependent potential. In the present work, the characteristic distance is corrected as being a hyperbolical temperature function and the potential well-depth is corrected as being a power function of temperature. The second virial coefficients of linear homonuclear molecules O_2, Cl_2, C_2F_6, and C_2H_6 are reproduced to test the modified 2CLJDQP model. The results show that the potential parameters cannot be considered as constant for the heavier molecules in large temperature range. In addition, the Lorentz–Berthelor mixing rule is modified into a temperature-dependent expression to calculate the second virial coefficients of heteronuclear molecules (such as CO, NO, CH_3F, CH_3Cl, CH_3CF_3, CH_3CHF_2, and CF_3CH_2F) and triatomic linear molecules (such as CO_2 and N_2O). It is shown that the calculated results from modified 2CLJDQP model are much better than those from 2CLJDQP model especially in the low temperature range. In this work, all the temperature corrections for potential parameters are from the fitting of second virial coefficients. The further work is needed to calculate the temperature correction from the quantum physics and molecular spectral data.

References

[1] Lucas K 2007 *Molecular Models for Fluids* (Cambridge: Cambridge University Press) pp. 266–283
[2] Chapman S and Cowling T G 1970 *The Mathematical Theory of Non-uniform Gases*, 3rd edn. (Cambridge: Cambridge University Press) pp. 226–276

[3] Boublik T, Nezbeda I and Hlavaty K 1980 *Statistical Thermodynamics of Simple Liquids and Their Mixtures* (Amsterdam: Elsevier Press) pp. 1–145
[4] Assael M J, Trusler J P and Tsolakis T F 1996 *Thermophysical Properties of Fluids* (London: Imperial College Press) pp. 37–46
[5] Poling B E, Prausnitz J M and O'connell J P 2001 *The Properties of Gases and Liquids*, 5th edn. (New York: McGraw- Hill Press) pp. 9.1–11.55
[6] Pai S J and Bae Y C 2013 *Fluid Phase Equilib.* **338** 245
[7] Pai S J and Bae Y C 2012 *Fluid Phase Equilib.* **317** 15
[8] Chiang K N, Chou C Y, Wu C J, Huang C J and Yew M C 2009 *ICCES* **9** 130
[9] Lennard-Jones J E 1924 *Proc. R. Soc. Lond. A* **106** 463
[10] Yeganegi S and Shadman M 2008 *Chem. Phys. Lett.* **451** 209
[11] Tokumasu T and Kamijo K 2004 *Superlattices Microstruct.* **35** 217
[12] Shukla K 1997 *Fluid Phase Equilib.* **27** 1
[13] Kronome G, Kristof T, Liszi J and Szalai I 1999 *Fluid Phase Equilib.* **155** 157
[14] Galbraith A L and Hall C K 2006 *Fluid Phase Equilib.* **241** 175
[15] Fotouh K and Shukla K 1997 *Fluid Phase Equilib.* **1** 35
[16] Takashi T, Taku O and Kenjiro K 2003 *Transactions of the Japanese Society of Mechanical Engineers* **B69** 1644
[17] Mecke M, Müller A and Winkelmann J 1997 *Int. J. Thermophys.* **18** 683
[18] Kohlera F and Nhuab N V 1993 *Mol. Phys.* **80** 795
[19] Kohler F, Quirke N and Perram J W 1979 *J. Chem. Phys.* **71** 4128
[20] Galbraith A L and Hall C K 2006 *Fluid Phase Equilib.* **241** 175
[21] Eslami H, Mozaffari F and Boushehri A 2001 *Int. J. Therm. Sci.* **40** 999
[22] Vega C, McBride C and Menduina C 2002 *Phys. Chem. Chem. Phys.* **4** 3000
[23] Meng L and Duan Y Y 2006 *Mol. Phys.* **104** 2891
[24] Zarkova L 1996 *Mol. Phys.* **88** 489
[25] Sweet R J and Steele A W 1967 *J. Chem. Phys.* **47** 3022
[26] Kong C L 1970 *J. Chem. Phys.* **53** 1516
[27] Murthy C S, Singer K and McDonald I R 1981 *Mol. Phys.* **44** 135
[28] Santisa A D and Frattinia D R 1987 *Mol. Phys.* **60** 21
[29] Meng L 2006 "Theorical and Experimental Study on the Virial Coefficients of Fluids" (Ph. D. Thesis) (Beijing: Tsinghua University) (in Chinese)
[30] Hu Y, Liu G J, Xu Y N and Tan Z M 1990 *Applied Statistical Mechanics-Basic for Thermal Physical Properties of Fluid* (Beijing: Chemical Industry Press) pp. 59–67 (in Chinese)
[31] Kriebel C, Mecke M, Winkelmann J, Vrabec J and Fischer J 1998 *Fluid Phase Equilib.* **142** 15
[32] Huang Y, Vrabec J and Hasse H 2009 *Fluid Phase Equilib.* **287** 62
[33] Boushehri A, Mason E A and Kestin J 1986 *Int. J. Thermophys.* **7** 1115
[34] Stefanov B 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 4519
[35] Hohm U, Zarkova L and Damyanova M 2006 *Int. J. Thermophys.* **27** 1725
[36] Al-Matar A K, Tobgy A H and Suleiman I A 2008 *Mol. Simul.* **34** 289
[37] Zarkova L and Pirgov P 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 4269
[38] Hirschfelder J O, Curtiss C F and Bird R B 1954 *Molecular Theory of Gases and Liquids* (New York: Wiley Press) p. 22–25
[39] Hohm U and Zarkova L 2004 *Chem. Phys.* **298** 195
[40] Damyanova M, Zarkova L and Hohm U 2009 *Int. J. Thermophys.* **30** 1165
[41] Zarkova L and Hohm U 2009 *J. Chem. Eng. Data* **54** 1648
[42] Wang S, Zhang Y and He M G 2012 *J. Eng. Thermophys.* **33** 199
[43] Matsumoto M and Nishimura T 1998 *ACM Trans. Mod. Comput. Simul.* **8** 3
[44] Contoy H 1967 *J. Chem. Phys.* **47** 5307
[45] Nezbeda I, Kolafa J and Labik S 1989 *Czech. J. Phys.* **B39** 65
[46] Delhommelle J and Millié P 2001 *Mol. Phys.* **99** 619
[47] Tsonopoulos C 1974 *AIChE J.* **20** 263
[48] Tsonopoulos C 1975 *AIChE J.* **21** 827
[49] Weber L A 1994 *Int. J. Thermophys.* **15** 461
[50] Meng L, Duan Y Y and Li L 2004 *Fluid Phase Equiliria* **226** 109