Theoretical study of the intermolecular potential energy and second virial coefficient in the mixtures of CH$_4$ and Kr gases: a comparison with experimental data

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The intermolecular potential energy surface (IPS) in the mixtures of CH$_4$–Kr gases from *ab initio* calculations has been explored. The *ab initio* calculation was performed at the second-order Møller–Plesset perturbation theory (MP$_2$), with the 6-311+G(2df,2pd) basis set, for three relative orientations of two CH$_4$–Kr molecules as a function of CH$_4$–Kr separation distance. In this work, the IPS, $U(r)$, of the CH$_4$–Kr complex has been investigated, where the vertex (V), edge (E) and face (F) of CH$_4$ approaches to Kr have been considered. Then, adjustable parameters of the Lennard-Jones and Buckingham potential energy function are fitted to the *ab initio* MP2/6-311+G(2df,2pd) interaction energies for three different orientations. Assuming a given set of parameters, we theoretically obtained second virial coefficients for the CH$_4$–Kr system, and compared with the experimental data at different temperatures. Trivial differences can be observed between the experimental and computational results.

Keywords: IPS; second virial coefficient; BSSE; MP$_2$

1. Introduction

The study of the intermolecular interaction in a chemical system can often lead to heavy numerical calculations in the form of *ab initio* quantum chemical methods or large-scale molecular dynamics and Monte Carlo simulations [1]. In this paper, we discuss these aspects to some extent, but intermolecular interactions can also be approached at a more descriptive level with a very modest amount of calculations done with paper and pen. The latter is a more fruitful approach for an ordinary chemist. Intermolecular interactions are of fundamental importance in understanding how atoms and molecules organise in liquids and solids. In the study of atomic and molecular forces, one can discard the forces whose effects do not coincide with molecular dimensions, i.e. gravitational forces are negligible. Only the forces with an electrostatic origin, arising from the interaction between electrons and nuclei in different molecules, are of interest for the present applications. Knowledge of the intermolecular interaction potential is the basis for understanding the properties of gases, liquids and solids. In principle, the evaluation of a macroscopic property such as the second virial coefficient of a moderately dense gas is straightforward if the intermolecular pair potential is accurately known [2]. The behaviour of molecular clusters linked by hydrogen bonds

is of special interest with a view to understanding a wide variety of chemical and biochemical problems [3]. Theoretical calculations provide detailed information about some aspects of the molecular interaction and the most likely structures for the clusters, which can rarely be accessed experimentally. *Ab initio* quantum mechanical calculations offer a way to obtain intermolecular potentials of molecules. This approach can be used to extract detailed information about the potential energy surface, which is sometimes difficult or practically impossible by other methods. Nevertheless, the quality of the potential is sensitive to the level of theory used for the calculation of interaction energies. Also, the basis set superposition error (BSSE) has a significant effect on the calculated interaction potential, and therefore it should be corrected [4]. *Ab initio* methods for calculating the intermolecular potential energy surface (IPS) have been reviewed by van der Avoird et al. [5] and van Lenthe et al. [6]. Also, many more studies have been reported on CH$_4$ complexes such as CH$_4$–He [7], CH$_4$–Ar [8], CH$_4$–H$_2$O [9], CH$_4$–HF [10], CH$_4$–NO [11] and CH$_4$–NO$^+$ [12]. The second virial coefficient (B_2) depends only on the pair interaction between the particles, the third virial coefficient (B_3) depends on two-body interactions and non-additive three-body interactions, and so on [1,4,13]. Also, the fifth virial coefficients for a system of hard disk have been studied by

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Kratky [14]. A basis set in chemistry is a set of functions used to create the molecular orbitals, which are expanded as a linear combination of such functions with the weights or coefficients to be determined. Usually, these functions are atomic orbitals, in that they are centred on atoms. Otherwise, the functions are centred on bonds or lone pairs. Pairs of functions centred on the two lobes of a *p*-orbital have also been used. Additionally, basis sets composed of sets of plane waves down to a cut-off wavelength are often used, especially in calculations involving systems with periodic boundary conditions, and the basis set effects for CF_4–CF_4, F_2–F_2, CH_4–CO complexes have been performed [15–17]. Theoretical studies of van der Waals complexes and intermolecular forces have been reviewed by Buckingham et al. [18]. In this work, the IPS, $U(r)$, of the CH_4–Kr complex has been investigated, where the vertex (V), edge (E) and face (F) of CH_4 approaches to Kr have been considered. To determine the IPS components, we used the Lennard-Jones and Buckingham potential formula. We theoretically estimated the second virial coefficients for the CH_4–Kr system and compared with the experimental data at different temperatures. All computations were done using the software Gaussian 98.

2.   Computational methods

In quantum chemistry, calculations of interaction energies are susceptible to the BSSE if they use finite basis sets. As the atoms of interacting molecules or two molecules approach one another, their basis functions overlap. Each monomer borrows functions from other nearby components, effectively increasing its basis set and improving the calculation of derived properties such as energy. If the total energy is minimised as a function of the system geometry, the short-range energies from the mixed basis sets must be compared with the long-range energies from the unmixed basis sets, and this mismatch introduces an error. Two methods exist to eliminate this problem. The first method is the chemical Hamiltonian approach (CHA) that replaces the conventional Hamiltonian with one designed to prevent the basis set from mixing *a priori*, by removing all the projector-containing terms which would allow basis set extension. The second method is the counterpoise approach (CP) that calculates the BSSE by reperforming all the calculations using the mixed basis sets, by introducing ghost orbitals, and then subtracts this error *a posteriori* from the uncorrected energy. Although conceptually very different, these two methods tend to give similar results.

In order to determine the potential energy surface, structures were fully optimised with the Møller–Plesset theory [19–21] for the system. Our estimates are only approximate but nevertheless interesting. The interaction energy, $U(r)$, for two systems A and B can simply be given as

$$U(r) = E_{AB}(A \dots B) - E_{AB}(A + B), \qquad (1)$$

where the arguments in parentheses indicate the basis set being used. $E_{AB}(A \dots B)$ is the energy of the $A \dots B$ system at the distance r, while $E_{AB}(A+B)$ is the energy of the two isolated components, at infinity ($r = \infty$). In *ab initio* calculations, the BSSE is of paramount importance [22]. This error can be eliminated to some extent by using the counterpoise correction (CPC) method [23]. In this method, both the physico-chemical compound $A \dots B$ and the A and B components at $r = \infty$ are calculated by using the full basis set for the $A \dots B$ system, hence

$$U = E_{AB}(A \dots B) - E_{AB}(A + B) + \Delta E_{CP}, \qquad (2)$$

where

$$\Delta E_{CP} = [E_A(A + B) - E_A(A \dots B)] + [E_B(A + B) \\ - E_B(A \dots B)]. \qquad (3)$$

The second virial coefficient, B_2, either obtained experimentally or estimated theoretically using the multi-dimensional interaction energy surface $U(r)$ (Equation (4)) can be used to determine the magnitude of these parameters [24],

$$B_2 = 2\pi N_A \int_0^\infty \left\{ 1 - \exp\left[-\frac{U(r)}{KT} \right] \right\} r^2 dr, \qquad (4)$$

where $U(r)$ is the intermolecular potential energy, N_A is the Avogadro constant and r is the separation distance of two molecules.

3.   Results and discussion

In this work, the computational procedures started with geometry optimisation of a CH_4 molecule at the MP_2 level of theory with the aug-cc-pvtz basis set. The bond length, bond angle and dihedral angle parameters explored by the *ab initio* method are listed in Table 1.

In order to determine the IPS, $U(r)$, of the CH_4–Kr system, the vertex (V), edge (E) and face (F) of CH_4 approaches to the Kr atom have been considered. A total of three different orientations of two CH_4–Kr molecules in the dimer relative to each other are shown in Figure 1.

Table 1.   The set of optimised parameters of CH_4 calculated at MP_2/aug-cc-pvtz.

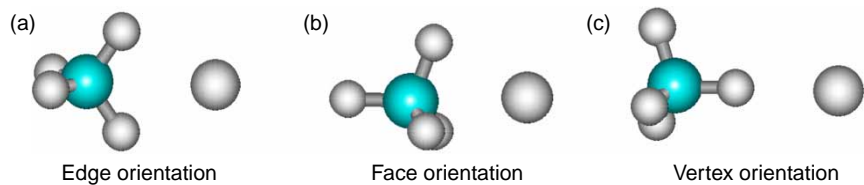| Optimised parameters	Value
C—H bond length	1.089 Å
HCH bond angle	109.4712°
HCHH dihedral angle	120°

Figure 1.   Three different orientations of Kr and CH$_4$.

Table 2.   IPS values of the three different orientations.

	Energy								
	Calculated by Gaussian (kcal/mol)			Fitted by LJ model (K)			Fitted by Buckingham model (kcal/mol)		
Distance (Å)	Edge	Face	Vertex	Edge	Face	Vertex	Edge	Face	Vertex
3.5	0.04997	0.6658	0.751062	−5.95053	341.6225	381.1407	0.105008	0.67303	1.780727
3.6	−0.15888	0.1079	0.580361	−107.2675	57.13709	294.2617	−0.091386	0.241566	1.214272
3.8	−0.35626	−0.14573	0.263267	−188.7531	−92.42187	136.6007	−0.310426	−0.12616	0.244444
4.0	−0.39749	−0.30464	0.065309	−195.2606	−159.8193	31.08185	−0.388855	−0.3064	0.076428
4.1	−0.39093	−0.33168	−0.06256	−186.9921	−168.0858	−35.63879	−0.397485	−0.34217	−0.043254
4.2	−0.37638	−0.33874	−0.14117	−175.4025	−167.5433	−73.60712	−0.393373	−0.35512	−0.12623
4.3	−0.36185	−0.33327	−0.19107	−162.2905	−161.7149	−99.81164	−0.380479	−0.35214	−0.181476
4.4	−0.33796	−0.32072	−0.21825	−148.7697	−152.8939	−112.0362	−0.361757	−0.33838	−0.21587
4.5	−0.30647	−0.3062	−0.23029	−135.5112	−142.5624	−116.1082	−0.339404	−0.31765	−0.234735
5.0	−0.18282	−0.19345	−0.20513	−81.51698	−91.21110	−100.3660	−0.216479	−0.18384	−0.223758
5.5	−0.10855	−0.11634	−0.12502	−48.66336	−55.79362	−61.69913	−0.119786	−0.07701	−0.132339
6.0	−0.06495	−0.07338	−0.07816	−29.70008	−34.44899	−39.38395	−0.058623	−0.01486	−0.068365
7.0	−0.0253	−0.035	−0.03639	−12.0673	−14.13166	−16.58835	−0.005566	0.026602	−0.004184

The IPS, $U(r)$, was calculated for different values of C–Kr separation, at the Møller–Plesset perturbation theory (MP$_2$), with the 6-311+G(2df,2pd) basis set. The MP$_2$/6-311+G(2df,2pd) calculation for the CH$_4$–Kr system has 150 basis functions and 230 primitive Gaussians. 6-311+G(2df,2pd) designates the 6-311G basis set supplemented by diffuse functions, two sets of the d function and one set of the f function on heavy atoms, and supplemented by two sets of the p function on hydrogen atoms and one set of the d function on heavy atoms. IPS values of the A, B and C orientations are listed in Table 2. The calculated $U(r)$ as a function of the C–Kr separation distance of the three different orientations is shown in Figure 2.
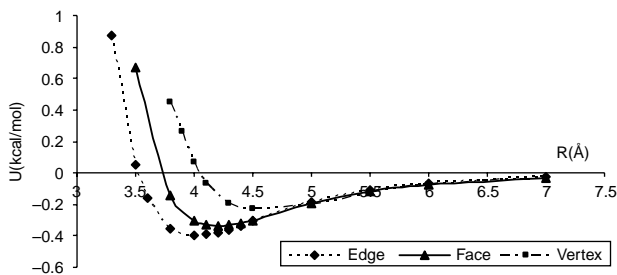

Figure 2.   The intermolecular potential energy obtained as a function of the C–Kr separation distance at MP$_2$/6-311+G(2df,2pd).

It can be seen from Figure 2 that all three orientations and separation distances of C–Kr have significant effects on the calculated potential energy curves (including position, depth and width of the potential well). Furthermore, the following trends with different distances can be deduced for the depth ($D_e = -E_{int}(R_e) = -E_{min}$) of the potential well of the calculated IPS.

It is evident from Figure 2 and Table 2 that the potential energy curves with the largest value of D_e are obtained with edge orientation, at the MP$_2$/6-311+G(2df,2pd) level of theory. The calculated IPS can further be compared based on the values of the position of the minimum point (R_e) of the potential curves. These quantities are very sensitive to different orientations and values of the separation distance of C–Kr used in the *ab initio* calculations. The values of D_e and R_e for the edge, face and vertex orientations at MP$_2$ with the 6-311+G(2df,2pd) basis set are 0.39749(4.0), 0.33874(4.2) and 0.23029(4.5), respectively. These quantities are very sensitive to the basis set used in the computations. For example, the values of D_e and R_e for the face orientation at MP$_2$ with aug-cc-pvdz, aug-cc-pvtz, aug-cc-pvqz and CBS basis sets are 0.332(3.95), 0.437(3.85), 0.489(3.80) and 0.529(3.80) and for the vertex orientation are 0.205(4.55), 0.273(4.40), 0.303 (4.35) and 0.326(4.35), respectively [25]. The energies

Table 3.   Adjustable parameters for the three different orientations fitted to the Lennard-Jones (12-6) potential and Buckingham potential model.

| Different orientations | Adjustable parameters | | | | |
| | Lennard-Jones potential | | Buckingham potential | | |
	ε/k (K)	σ (Å)	A	B	C
Edge	197.62	3.496	− 222.37632	1.156211	7338.3369
Face	168.7	3.688	− 508.9033	1.2356383	13620.493
Vertex	116.4	4.041	− 264.51286	1.0996622	13632.854

below the asymptote are given in kcal/mol. The values in parentheses correspond to the C–Kr distance in Å.

In this work, to estimate the IPS, $U(r)$, for the CH_4–Kr system, we used the Lennard-Jones (12-6) (Equation (5)) and Buckingham potential (Equation (6)) model, which can be expressed as

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \qquad (5)$$

$$U(r) = A \exp(-Br) + \frac{C}{r^6}, \qquad (6)$$

where A, B and C are adjustable parameters of the Buckingham potential [25], and ε and σ are the Lennard-Jones energy and size parameters, respectively, and r is the separation distance of C–Kr. Then, the adjustable parameters A, B, C and (ε, σ) are fitted to the *ab initio* $MP_2/6$-$311+G(2df,2pd)$ interaction energies for the three different orientations. The values of the adjustable potential parameters for the three different orientations are listed in Table 3. In addition, the curves of *ab initio* IPSs are fitted to the Lennard-Jones (12-6) and Buckingham potential, as shown in Figure 3. The location and depth of wells along the edge, face and vertex approaches are fitted to the Buckingham potential at $MP_2/6$-$311+G(2df,2pd)$ are 0.39748(4.1), 0.35512(4.2) and 0.23473(4.5) and at fp-CCSD(T)/CBS are 0.43(4.01), 0.47(3.87) and 0.32(4.40), respectively [25]. Potential energies are given in kcal/mol. The values in parentheses correspond to the C–Kr distance in Å. So, in this work, we have shown that it is possible to obtain a potential function, $U(r)$, for the CH_4–Kr system by quantum mechanical calculations. Therefore, from the known $U(r)$ formula, we can theoretically estimate the second virial coefficients, B_2, for the CH_4–Kr system by quantum mechanical calculations. The second virial coefficients were calculated using Equation (4); calculations were performed for a range of different experimental temperatures that are listed in Table 4. The calculated and experimental [26] values of the second virial coefficients are plotted in Figure 4 and are shown for selected temperatures in Table 4. After the calculations of the second virial

coefficients for different temperatures and its comparison with the experimental values, trivial differences can be observed between the experimental and computational results.
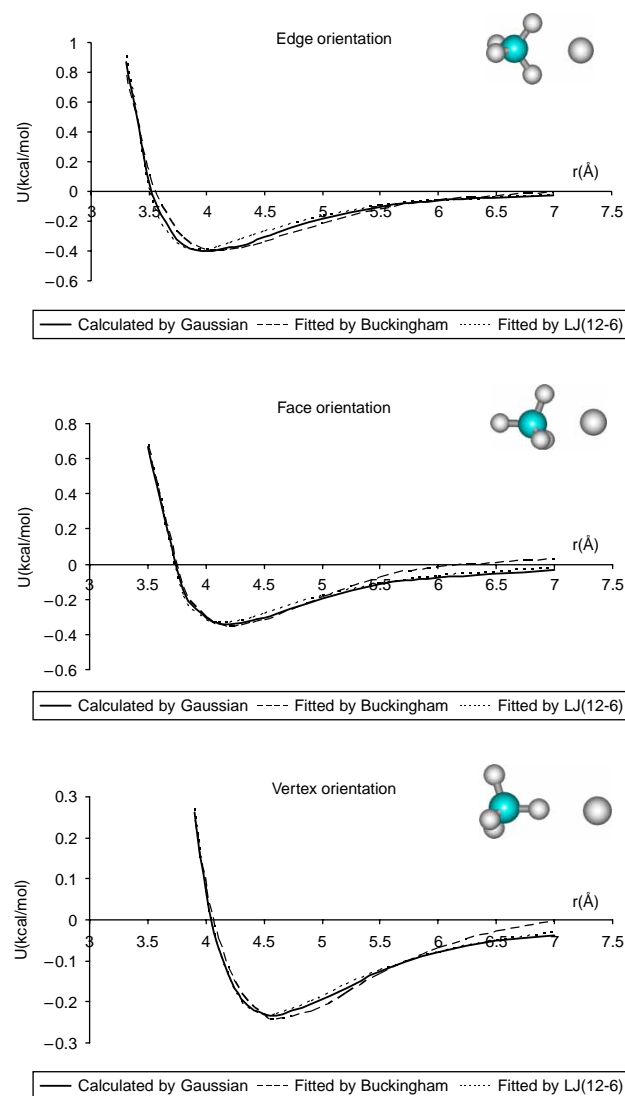

Figure 3.   The CH_4–Kr intermolecular potential energy interactions obtained at $MP_2/6$-$311+G(2df,2pd)$ are fitted to the Lennard-Jones (LJ) (12-6) and Buckingham potential model.

Table 4.   Second virial coefficients calculated from the *ab initio* potential for selected experimental temperatures.

|		B_2 (cm^3/mol)						
		Edge			Face		Vertex	
T (K)	B (exp)	B (cal)	$\lvert(B_{exp} - B_{cal})/B_{exp}\rvert \times 100$	B (cal)	$\lvert(B_{exp} - B_{cal})/B_{exp}\rvert \times 100$	B (cal)	$\lvert(B_{exp} - B_{cal})/B_{exp}\rvert \times 100$
118.65	−297.2	−333.614	−12.25235532	−295.526	0.563257066	−204.289	31.26211306
121.05	−286.3	−321.742	−12.37932239	−285.354	0.330422634	−197.244	31.10583304
125.38	−268.2	−302.06	−12.62490679	−268.403	−0.075689784	−185.405	30.87061894
132.08	−243.9	−275.361	−12.89913899	−245.23	−0.545305453	−169.017	30.70233702
141.22	−213.9	−244.818	−14.45441795	−218.459	−2.131369799	−149.78	29.97662459
152.18	−185.3	−214.969	−16.01133297	−192.014	−3.623313546	−130.448	29.60172693
166.44	−157.1	−184.139	−17.21133036	−164.395	−4.643539147	−109.896	30.04710376
182.13	−137.6	−157.609	−17.09435364	−140.37	−4.286775632	−91.7091	31.86545319
200.44	−112.1	−133.436	−19.03300624	−118.266	−5.50044603	−74.7182	33.34683318
221.55	−91.7	−111.826	−21.9476554	−98.3287	−7.22868048	−59.1809	35.46248637
225.96	−86.8	−107.954	−24.37096774	−94.7388	−9.146082949	−56.362	35.06682028
245.67	−73.8	−92.7525	−25.68089431	−80.5917	−9.202845528	−45.1917	38.76463415
270.82	−60.6	−77.2584	−27.48910891	−66.087	−9.054455446	−33.6398	44.48877888
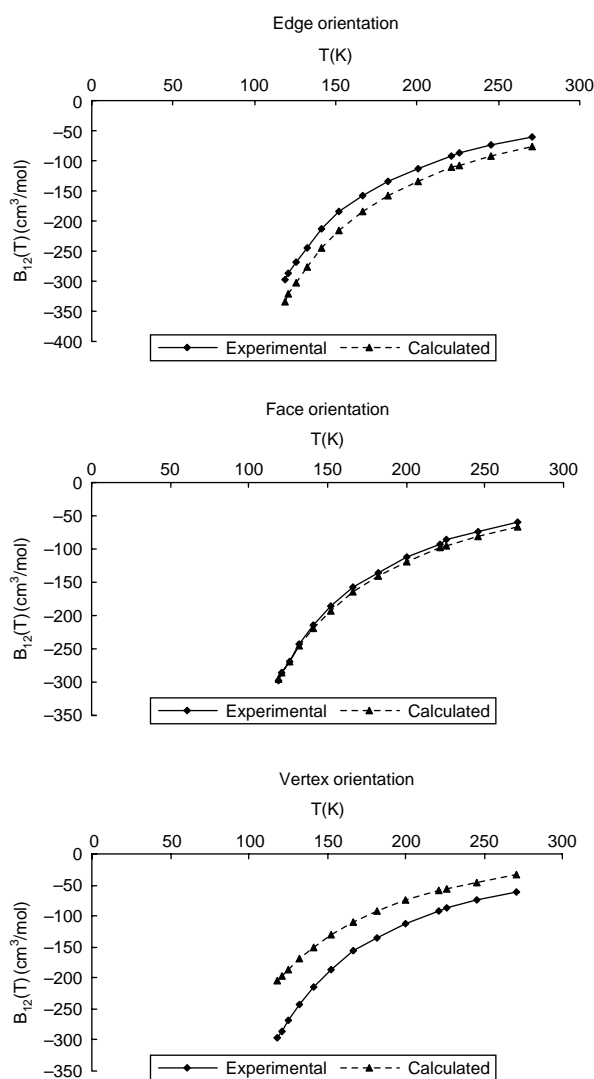
Figure 4.   Comparison between the computational and experimental data of the second virial coefficients for selected experimental temperatures.

4.   Conclusion

We have studied the interaction potentials between the Kr and CH$_4$ molecules. Our calculations were made using the MP$_2$ methods and 6-311+G(2df,2pd) basis set. Moreover, the dependence of the potential energy surface on the rare gas is analogous to that in the counterpart rare gas–CH$_4$ systems [25]. Investigation of the dependence of the intermolecular potential energy curves on the *ab initio* levels and basis sets between the approaching Kr–CH$_4$ was studied by Alexander and Troya [25]. Addition and reduction of the potential energy by distance changing from far to near; on the other hand, the depth of the potential well in the case of two approaching molecules is lower than the state of two approaching atoms or one atom and a molecule in order to form a bond. Generally, by increasing the distance of approach of two molecules and the attractive force between them, the depth of the potential well is increased. Thus, with respect to Figure 2, in the edge state, the spatial intruding of hydrogen atoms of CH$_4$ for approaching Kr is rather lower than that in the face and vertex states, which results in the weak overlap of electron clouds. Thus, two more molecules can approach each other more closely, and if they are located at the proper distance from each other, one of the molecules can induce a dipole moment and inductive dipole moment in the neighbouring molecule, which leads to the generation of the London attraction between them. Therefore, it releases more energy towards other states and increases the depth of the potential well. In this work, we have estimated the IPSs for the CH$_4$–Kr system using the Lennard-Jones and the Buckingham potential models, to obtain the adjustable parameters of potential equations and theoretically estimate the second virial coefficients. Figure 3 depicts a comparison of our best fitting estimates of the intermolecular potential energy curves for the Kr–CH$_4$ pairs along the edge, face and vertex approaches.

The location and depth of wells along the edge, face and vertex approaches fitted to the Buckingham and Lennard-Jones potential and calculated by Gaussian at $MP_2/6\text{-}311+G(2df,2pd)$ are 0.39748, 0.37159, 0.39093(4.1), 0.35512, 0.33294, 0.33873(4.2) and 0.23473, 0.23072, 0.23029(4.5), respectively. Potential energies are given in kcal/mol. The values in parentheses correspond to the C–Kr distance in Å. Trivial differences can be observed between the inter-molecular potential energy fitted to the Buckingham and Lennard-Jones potential and computational results. Considering Figure 4, firstly, the temperature dependence of the second virial coefficient is specified completely. Secondly, after the second virial coefficient calculations for different temperatures and comparison with its experimental values, trivial differences between the experimental and computational values are observed, also at low temperatures, the portion of that state in which there is no spatial intruding (edge) is more than the others.

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