Using graphene to simplify the adsorption of methane on shale in MD simulations

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In this paper, we explored material similarity between graphene and shale for methane (CH₄) adsorption in the shale gas recovery simulations. The reasons of choosing graphene to model shale have been clarified. Through theoretical analysis, we obtained the attenuation law of interaction potential between CH₄ and multilayer graphene. It indicates the adsorption energy of CH₄ on monolayer graphene is closest to that on shale. The limiting heat of adsorption of CH₄ on graphene was calculated by molecular dynamics (MD) simulation. The adsorption isotherms and adsorption heats on the monolayer graphene, whose width of the slit pore ranges from 2 nm to 11 nm, were calculated by using grand canonical Monte Carlo (GCMC) simulations at different temperatures. The computed adsorption heat is validated by experimental data, which indicates that the adsorption properties of CH₄ on shale are quite similar with that of CH₄ on graphene. Our study may provide a direct evidence of using graphene in modeling shale in simulating the shale gas adsorption/desorption.

1. Introduction

As a unconventional gas resource, shale gas plays an increasingly important role in renewable energy, because of its great reserves throughout the world and its clean when burned [1,2]. Most shale gas production in North America attributes to the development of horizontal drilling and fracking technology [3,4]. Also shale gas has been extensively explored in Australia, Europe and China in recent years [5]. Even though thousands of shale gas wells are in production around the world, there are still many difficulties in shale gas exploitation technology [6–10], and the thermodynamic properties of shale gas are still poorly understood. Hence, researchers have increasingly tried to explore the properties of shale gas and find out an efficient way in enhancing shale gas recovery (ESGR) [11–14]. Experiment is a direct way to explore the properties of shale gas and find out an efficient way in enhancing shale gas recovery (ESGR) [11–14]. Experiment is a direct way to explore the properties of shale gas and find out an efficient way in enhancing shale gas recovery (ESGR) [11–14]. Experiment is a direct way to explore the properties of shale gas and find out an efficient way in enhancing shale gas recovery (ESGR) [11–14]. Experiment is a direct way to explore the properties of shale gas and find out an efficient way in enhancing shale gas recovery (ESGR) [11–14]. Experiment is a direct way to explore the properties of shale gas and find out an efficient way in enhancing shale gas recovery (ESGR) [11–14]. Experiment is a direct way to explore the properties of shale gas and find out an efficient way in enhancing shale gas recovery (ESGR) [11–14].

In previous simulations, CH₄ was considered under thermodynamic equilibrium in three-dimensional periodic orthorhombic pore geometry consisting of upper and lower pore-walls made of graphene [25]. Coal and shale both require a thorough understanding of the CO₂ adsorption properties in microporous carbon-based materials. Wilcox et al. investigated the adsorption of CO₂ in microporous carbons. They explored CH₄ adsorption properties on graphitic surfaces as an initial model of coal and kerogen of gas shale [26,27]. The adsorption behavior of oil within nanoscale carbonaceous slits of shale systems was studied by using MD simulation, with graphene sheets as the model of shale [28]. Recently, the atomic mechanisms and adsorption properties of CH₄ on graphene (or carbon nanopores) have been inves-
tigated [29–32]. Graphene is widely used in the researches of shale and coal. Even though many researchers chose graphene as a model of shale or coal, the reasons for this choice are not clear or the evidence remains insufficient. Hence, material similarity between graphene and shale for CH4 adsorption need to be explored in detail.

In this paper, thermodynamic properties of the CH4 adsorption on graphene are investigated and the results are compared with the experiment. Firstly, we used theoretical analysis to investigate the interaction potential between CH4 and graphene, the effect of the number of graphene layers on the interaction potential was explored. Secondly, we provide a way to calculate the limiting heat of adsorption of CH4 on graphene, and compared the limiting heat with experimental results. Thirdly, the grand canonical Monte Carlo (GCMC) simulations were performed to predict the CH4 adsorption isotherm at 300 K, 320 K, 340 K and 360 K, and the fugacity from 1 MPa to 40 MPa, with 2 nm, 3 nm, 5 nm, 7 nm, 9 nm and 11 nm slit pore sizes. And we provide a way to transform fugacity and absolute adsorption into pressure and excess adsorption. Finally, the isoteric adsorption heats of CH4 on graphene at multiple graphene slit pore sizes at different temperatures were investigated. Our results and related analyses may help to understand the CH4 adsorption on graphene. More importantly, the results provide a strong evidence of using graphene in modeling shale in simulating the shale gas adsorption/desorption. This study aims to quantify whether graphene may be used to represent the wall boundaries of nanopores in shale gas adsorption measurements in MD simulations. It presents future researchers to simplify the description of shale nanostructure with an equivalent slit pore consisting of graphene.

2. Methods

MD simulations implemented in LAMMPS [33] have been carried out. We simulated the limiting adsorption heat of CH4 on graphene adopting consistent valence force-field (CVFF) [34], which is based on the ab initio calculations and experiments. The total potential energy consists of the bond energy $E_b$, and nonbond energy $E_n$. $E_b$ is the sum of bond and angle energy. $E_n$ is the interaction potential between two atoms i and j, which is Lennard-Jones (LJ) energies:

$$E_{ij} = 4\varepsilon_{ij} \left[\left(\frac{r_{ij}}{\sigma_{ij}}\right)^{12} - \left(\frac{r_{ij}}{\sigma_{ij}}\right)^{6}\right],$$

where $\varepsilon_{ij}$ is the depth of the potential well, $\sigma_{ij}$ is the zero-crossing distance for the potential, $r_{ij}$ is the distance between the two atoms. The values of $\sigma_{ij}$ and $\varepsilon_{ij}$ between two species were calculated by the Lorentz-Berthelot (LB) rule: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$. The whole system was modeled in NVT ensemble (constant number of atoms, volume and temperature) with Nose/Hoover method and the time step was 1 fs, to regulate the temperature at 300 K. The vdw interactions in these simulations were calculated with a cutoff of 12.5 Å, and the electrostatic interactions were described by Ewald method and the cutoff is 12.5 Å. In our simulations, it was fugacity rather than pressure that was used for predicting adsorption isotherms, adsorption heat and other thermodynamics properties.

3. Results and discussions

3.1. Limiting heat of adsorption of CH4 on graphene

When the amount adsorbed approaches zero, the isosteric heat of adsorption is called the limiting heat of adsorption. It is a representative thermal effect of the adsorption. The limiting heat of adsorption can be evaluated from Henry constants if they are available for several temperatures, and the Henry constant varies with temperature following the van’t Hoff equation [35]:

$$\frac{d \ln K}{dT} = \frac{\Delta H_0}{RT^2},$$

where $K$ is the Henry constant, $T$ is the absolute temperature, $\Delta H_0$ is the difference of molar enthalpy between adsorption states and gas states, $R$ is the ideal gas constant. The limiting heat of adsorption is $-\Delta H_0$. Integrating Eq. (2), we can obtain

$$\ln K = -\frac{\Delta H_0}{RT} + C.$$ (3)

Hence, by plotting the variation of $\ln K$ with $1/T$, the limiting heat of adsorption can be evaluated from the slope of the plot. This method is widely used in experiment for evaluating the limiting heat of adsorption.

However, as for simulations in this case, we found a direct way to calculate the limiting heat of adsorption. In the analysis of adsorption process, it is necessary to distinguish adsorbed molecules from gas phase. For the convenience of thermodynamic analysis, Gibbs defined a mathematical dividing surface between the gas phase and adsorbent as shown in Fig. 1. According to the Gibbs model of adsorption, any extensive thermodynamics quantity $X$ may be written as the sum of the gas phase, the adsorbate and the adsorbent:

$$X = X^g + X^s + X^i.$$ (4)

After adsorbing on the adsorbent, the total internal energy $U$ of solid phase is

$$U = TS - pV + \sum_{i=1}^{c} \mu_i n_i + \mu,$$ (5)

where $S$ is entropy, $p$ is the pressure, $\mu_i$ and $n_i$ are the chemical potential and the number of moles of adsorbate $i$, respectively, $\mu$.
is the chemical potential of the solid adsorbent. For the adsorbent in its pure standard state at the same pressure and temperature, the total internal energy \( U^o \) of solid phase is
\[
U^o = TS^o - pV^o + \mu^o.
\]

Hence, the extensive quantities of the adsorption phase are obtained
\[
U^a = U - U^o
\]
\[
S^a = S - S^o
\]
\[
\eta_i^a = \eta_i
\]
\[
V^a = V - V^o = 0,
\]
the volume \( V^a \) of adsorption phase is zero for the Gibbs dividing surface. Subtracting Eq. (6) from Eq. (5), and substituting Eq. (7), the internal energy \( U^a \) of the adsorption phase is obtained
\[
U^a = TS^a + \sum_{i=1}^c \mu_i \eta_i^a + \psi,
\]
where \( \psi = \mu - \mu^o \) is the surface potential. The surface potential is zero when no adsorption occurs.

The enthalpy of a system is defined as
\[
H = U + pV.
\]
From Eqs. (8), (9) and \( V^a = 0 \)
\[
H^a = TS^a + \sum_{i=1}^c \mu_i \eta_i^a + \psi + pV^a
\]
\[
= TS^a + \sum_{i=1}^c \mu_i \eta_i^a + \psi.
\]
From Eqs. (8) and (10)
\[
U^a = H^a.
\]
Before the adsorption happening, the internal energy \( U_0 \) and the enthalpy \( H_0 \) of adsorption phase are zero. Hence, the total internal energy \( U_t \) and the total enthalpy \( H_t \) are obtained
\[
U_0 = U_0^t + U_0^f = U_0^f + U_0^t
\]
\[
H_0 = H_0^t + H_0^f + H_0^s = H_0^s + H_0^t.
\]
After adsorption, the total internal energy \( U_t \) and the total enthalpy \( H_t \) are obtained
\[
U_t = U_t^a + U_t^f + U_t^g
\]
\[
H_t = H_t^a + H_t^f + H_t^g.
\]
 Subtracting Eq. (12) from Eq. (13), and using Gibbs model, \( U_t^a - U_0^a \) and \( H_t^a = H_0^a \), we have
\[
\Delta U = U_t - U_0 = U_t^a + U_t^f - U_0^a
\]
\[
\Delta H = H_t - H_0 = H_t^a + H_t^f - H_0^a.
\]
From Eqs. (9), (11) and (14), we have
\[
\Delta H = \Delta U + (p_t^f - p_0^f) V^f.
\]

The limiting heat of adsorption is the isosteric heat at pressure tends zero \( p_t^f \to 0 \). Hence, \((p_t^f - p_0^f) \to 0\), and \( V^f \) is a finite constant. Eq. (15) can be transformed into
\[
\Delta H_{\text{lim}} = \Delta U.
\]
Hence, in this case, in order to obtain the limiting heat of adsorption we just need to calculate the change in internal energy of CH4 adsorption on graphene. The variations of the internal energy of CH4 adsorption on monolayer and bilayer graphene were simulated as shown in Fig. A.2. The change in internal energy of CH4 adsorption on monolayer graphene is \(-5.97\) kcal/mol, and when CH4 adsorption on bilayer graphene, it becomes \(-6.38\) kcal/mol. The limiting heat of adsorption is \(-\Delta H_{\text{lim}} = -\Delta U\), hence the limiting heat of CH4 adsorption on bilayer graphene is larger than adsorption on monolayer graphene.

Experimentally, the isosteric heat of adsorption of CH4 on Woodford shale is 5.23 kcal/mol [36]. The limiting heat of adsorption of CH4 on shale is 5.72 kcal/mol [37]. Comparing the CH4 adsorption on monolayer graphene with the CH4 adsorption on shale, the limiting heat of adsorption is very close, and the isosteric heat of adsorption on CH4 on Woodford shale is lower than the limiting heat of adsorption of CH4 adsorption on monolayer graphene. It is a reasonable approximation by showing that CH4 adsorption heat on graphene is similar to that obtained from macroscale experiments on shale. Therefore, it is feasible to investigate the adsorption properties of CH4 on graphene instead of the adsorption on shale in simulations.

3.2. Adsorption isotherm of CH4 on graphene

The GCMC simulations were performed to predict the CH4 adsorption isotherm at 300 K, 320 K, 340 K and 360 K, in fugacity from 1 MPa to 40 MPa, with 2 nm, 3 nm, 5 nm, 7 nm, 9 nm and 11 nm slit pore sizes, respectively. The density fields of CH4 at 300 K in the 2 nm slit pore size in different fugacity are shown in Fig. 2. It shows that CH4 adsorbed on the graphene firstly in low fugacity, and then the free CH4 molecules increase with the increasing fugacity. The CH4 adsorption isotherms for multiple graphene slit pore sizes at different temperatures are shown in Fig. 3.

From these results, we found that adsorbed amounts increase with the decrease of the temperature at the same slit pore size of graphene, and decrease with increasing slit pore size of the graphene. The isotherms in these simulations conform to Langmuir adsorption behavior. It indicates that the CH4 adsorption on the graphene is monolayer adsorption. Therefore, we fit the isotherms with Langmuir equation [38]
\[
q = q_m \frac{kp}{1 + kp},
\]
where \( q \) is the equilibrium adsorption capacity, \( q_m \) is the saturated adsorption capacity, \( k \) is the Langmuir equilibrium constant in 1/MPa. The fitting parameters are shown in Table 1. The saturated adsorption capacity decreases with the increasing temperature, but it increases with the increasing slit pore size of graphene. As shown in Fig. 4, the Langmuir equilibrium constant decreases with the increasing slit pore size of graphene. The larger the Langmuir equilibrium constant becomes, the stronger the adsorption capacity between adsorbate and adsorbent is. It means that the CH4 molecules much more easily adsorb in the smaller slit pore. In addition, the Langmuir equilibrium constant decreases with the increasing temperature. As the temperature increases, the kinetic energy of the adsorption CH4 increases. This increase leads to the CH4 much easier desorption from the graphene.

In this work the adsorbed amount is the absolute adsorption, which is composed of adsorption phase and gas phase. However, excess adsorption is widely used in the experiment. The excess adsorption is defined as
\[
q_e = q - \frac{pV}{M},
\]
where \( q \) is the adsorption in mol, \( \rho \) is the density of free phase, \( \nu \) is the free volume, \( M \) is the molar mass of the gas. Compressibility factor is a useful property for modifying the idea gas law to account for the real gas. In statistical mechanics the description of compressibility factor is
Fig. 2. The density field of CH₄ at 300 K in different fugacity. (a) 1 MPa, (b) 3 MPa, (c) 8 MPa.

Fig. 3. The adsorption isotherms of CH₄ in multiple graphene slit pore sizes at different temperatures. (a) 2 nm, (b) 3 nm, (c) 5 nm, (d) 7 nm, (e) 9 nm, (f) 11 nm. The dots are simulated results. The black lines are the fitting by Langmuir equation.
In order to obtain the excess adsorbed amount, we need to know the compressibility factor and fugacity coefficient.

The chemical potential \( \mu' \) is equal to the molar Gibbs free energy, and for a simple compressible substance we have

\[
d\mu' = dG = vdp - sdT.
\]

In the isothermal process, it becomes

\[
d\mu' = vdp.
\]

The total differential of chemical potential of a pure real gas is defined as

\[
d\mu'_\text{real} = RTd \ln f.
\]

Combining Eq. (24) with Eq. (25) we get

\[
d \ln f = \frac{vdp}{RT}.
\]

The total differential of Eq. (21) is

\[
d \ln \phi = d \ln f - d \ln p.
\]

Integration of Eq. (27) from zero to a state pressure \( P \) and replace the definition of \( Z \) factor in it, we obtain

\[
\ln \phi = \int_0^P \left[ \frac{\mu}{RT} \frac{1}{P} \right] dp = \int_0^P Z - \frac{1}{P} \ dp.
\]

In addition, based on a virial equation of state, the approach to establishing \( Z(T, P) \) is

\[
Z(T, P) = 1 + a(T)P + b(T)P^2 + c(T)P^3 + \cdots,
\]

where \( a(T) \) and \( b(T) \) are related to the temperature of \( CH_4 \). Hence, these coefficients, in different temperature, can be fitted by

\[
p = n(1 + ap + bp^2 + cp^3)RT.
\]

We chose the first three orders of virial equation of state. Then the integral in Eq. (28) can be evaluated

\[
\ln \frac{P}{p} = \int_0^P \left[ \frac{Z - 1}{P} \right] dp = \int_0^P \frac{ap + bp^2 + cp^3}{p} dp
\]

\[
= ap + \frac{bp^2}{2} + \frac{cp^3}{3}.
\]

It can be written as

\[
f = pe^{ap + \frac{bp^2}{2} + \frac{cp^3}{3}}.
\]

The fitting results, \( CH_4 \) in 300 K, 320 K, 340 K and 360 K with pressure from 1 MPa to 10 MPa, are shown in Fig. 5. Hence, we can plot the function of Eq. (32) with the fitting coefficients as shown in Fig. 6.

By numerically solving Eq. (32), we can transform the fugacity to pressure. And then we obtain the excess adsorption with the pressure \( p \) and the corresponding absolute adsorption \( q \) by Eq. (20). Hence, the relationship between fugacity and absolute adsorption can be turned into pressure and excess adsorption. The excess adsorption isotherms of \( CH_4 \) in 2 nm slit pore size graphene at 300 K, 320 K, 340 K and 360 K are shown in Fig. 7. Therefore, the results of simulation and experiment can be compared. From these results we found that excess adsorbed amount increases with the decrease of the temperature in 2 nm slit pore size of graphene. And the excess adsorption cannot be obviously improved when the pressure more than 11–12 MPa. It has the same tendency in the model of kerogen from the Woodford and Green River shale samples [39]. Experimentally, the excess adsorbed amount increases at first and then stop increasing after 11–12 MPa in Tarrant A-3 shale and Blakely #1 shale [36]. Through the comparison of the experimental and simulative results, their changing tendency is in agreement qualitatively. Therefore, it also shows that it is feasible to choose graphene as a model of shale in simulations. In addition, the simulation results can give an instruction to product directly.

### Table 1

Adsorption parameters with Langmuir fitting.

| nm | qₑ (mol/m³) | k (MPa⁻¹) |
|-----|-------------|------------|
|     | 300 K       | 320 K      | 340 K      | 360 K      |
| 2   | 17287.53    | 16625.94   | 15829.30   | 15241.14   | 0.290   | 0.242 | 0.217 | 0.188 |
| 3   | 18484.64    | 17470.77   | 16841.23   | 15829.66   | 0.127   | 0.115 | 0.107 | 0.097 |
| 5   | 21269.87    | 20555.29   | 18745.23   | 17527.62   | 0.061   | 0.054 | 0.054 | 0.053 |
| 7   | 23808.51    | 22249.17   | 20902.78   | 19541.45   | 0.043   | 0.040 | 0.038 | 0.037 |
| 9   | 25811.14    | 23818.53   | 22258.98   | 21618.39   | 0.035   | 0.034 | 0.032 | 0.029 |
| 11  | 27660.88    | 25832.49   | 24118.11   | 22563.85   | 0.030   | 0.028 | 0.027 | 0.026 |

**Fig. 4.** Variations of the Langmuir equilibrium constant.
3.3. Isosteric adsorption heat of CH$_4$ on graphene

Isosteric adsorption heat is commonly used in the characterization of gas adsorption. The isosteric adsorption heats of CH$_4$ in multiple graphene slit pore sizes at different temperatures were shown in Fig. 8. The graph’s horizontal axis shows the absolute adsorption; hence, the adsorption heat decreased at first and later flattened particularly evident in 3–11 nm pores. It indicates that the adsorption heat decreases with increasing coverage. Actually, the adsorption heat is independent of coverage in ideal adsorption. But for real adsorption, adsorption heat changes with coverage because of the surface heterogeneity. In the beginning, CH$_4$ adsorbs at the active adsorption site which gives out more heat than the CH$_4$ adsorbs at the inactive adsorption site.

From these results, we found that the adsorption heat of CH$_4$ in 2 nm slit pore size graphene almost unchanged when the absolute adsorption increase. Because the 2 nm pore is so small that the CH$_4$ molecules can easily adsorb at the graphene surface and then quickly reach saturation. In addition, the adsorption heat decreases with the increasing slit pore size of graphene, which means that the adsorption capacity of smaller pore is stronger than larger pore. This property is consistent with the experimental result [40]. Moreover, the adsorption heat decreases with increasing temperature.
Because the higher the temperature becomes, the faster the motion of the molecule is. So the adsorption capacity decreases with the increasing temperature.

4. Conclusions

For the first time, the interaction potential between multilayer graphene and CH4 were investigated. The results indicate that the first two layers of graphene play the main role of the interaction potential between multilayer graphene and CH4. We can just consider investigating the interaction between CH4 with monolayer graphene (85.5%) or bilayer graphene (96.6%). The limiting heat of CH4 adsorption on monolayer graphene is 5.97 kcal/mol, and that of CH4 adsorption on bilayer graphene becomes 6.38 kcal/mol. The limiting heat of adsorption on monolayer graphene is very close to the adsorption heat with the CH4 adsorption on shale. Therefore, it proves that it is feasible to investigate the adsorption properties of CH4 on graphene instead of adsorption on shale in simulations.

We found that adsorbed amount increases with the decrease of the temperature at the same slit pore size of graphene, and decrease with increasing slit pore size of the graphene. The Langmuir equilibrium constant decreases with the increasing slit pore size of graphene. Hence, CH4 is much easier to be adsorbed in the smaller pore. In addition, the Langmuir equilibrium constant decreases with the increasing temperature. The adsorption heat decreases with increasing temperature because the higher the temperature becomes, the faster the motion of the molecule is. So the adsorption capacity decreases with the increasing temperature. Based on theoretical analysis, we provide a way to transform fugacity and absolute adsorption into pressure and excess adsorption, respectively, which is convenient for combining simulation and experiment. These results show good accordance with existing experiments and could help to understand the shale gas adsorption on shale. Consequently, graphene can be a good candidate as a model of shale in simulations.

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Appendix A. Interaction potential between CH4 and graphene

The interaction between CH4 and graphene is LJ potential:

\[ E(r) = 4e \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]. \tag{A.1} \]

where \( e \) is the well depth, \( \sigma \) is the value of \( r \) at which \( E(r) = 0 \). The number density of the graphene surface is \( \rho = N/S = 3.8 \times 10^{19} \text{ m}^{-2} \) (number of particles \( N \) divided by the surface area \( S \)). Here, the total interaction between single atomic layer and adsorbate is

\[ E(z) = \rho \int_{0}^{z} \int_{0}^{\infty} \left[ 4\varepsilon \sigma^{12} (r_{0}^{6} + z^{6})^{-6} - 4\varepsilon \sigma^{6} (r_{0}^{3} + z^{3})^{-3} \right] r_{0} \, dr_{0} \]

\[ = 8\varepsilon\pi\rho\sigma^{2} \left( \frac{\sigma^{12}}{10\varepsilon^{12}} - \frac{\sigma^{6}}{4\varepsilon^{6}} \right). \tag{A.2} \]

where \( z \) is the adsorption distance, \( r_{0} \) is the distance from the center. In order to investigate the effect of the number of graphene layers on the interaction potential, we have explored the CH4 adsorbs on multilayer graphene as shown in Fig. A.1. Hence, the interaction between 1st layer and a molecule is
Fig. A1. CH$_4$ adsors on multilayer graphene. $z_0$ is the adsorption distance, $h_0$ is the distance from the center, $d$ is the space between bilayer of graphene.

Fig. A2. Variations of the internal energy in the CH$_4$ adsorption processes. The black line is the case of monolayer graphene. The red line is the case of bilayer graphene. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$E_1 = \frac{8\pi \varepsilon \rho \sigma^2}{10 \pi^2} \left( \frac{\sigma^4}{4 \pi^2} \right).$$

(A.3)

The interaction between nth layer and a molecular is

$$E_n = \frac{8\varepsilon \pi \rho \sigma^2}{16 \pi^2} \left( \frac{\sigma^4}{4 \pi^2} \right).$$

(A.4)

Therefore, the total interaction between multilayer graphene and a CH$_4$ is $E_{\text{total}} = \sum_{i=1}^{N} E_i$. The parameter $\sigma$ is 3.68 Å. The equilibrium distance between CH$_4$ and graphene $z_0$ is 3.49 Å. And the space between bilayer graphene $d$ is 3.6 Å. Hence, we have $E_1/E_{\text{total}} \approx 85.5\%$ and $(E_1 + E_2)/E_{\text{total}} \approx 96.6\%$. The results indicate that the first bilayer of graphene plays the main role of the interaction potential between multilayer graphene and CH$_4$. Hence, if we want to explore the adsorption properties of CH$_4$ on multilayer graphene, we can just consider investigating the interaction between CH$_4$ and monolayer or bilayer graphene. The variations of the internal energy of CH$_4$ adsorption on monolayer and bilayer graphene were simulated as shown in Fig. A2.

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