

The Determination of Shale Gas Absolute Adsorption Basing on Molecular Dynamics Simulation

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Abstract: The adsorption experimental isotherms developed for excess adsorption of supercritical gases with the appearance of a distinct maximum and quick decrease cannot be explained with the base of the classic adsorption theory developed for absolute adsorption. The key of describing the adsorption of supercritical gases with classical adsorption theory is the correct conversion of the quantity of absolute adsorption and excess adsorption. According to Gibbs definition of adsorption, accurate evaluation of the adsorbed phase density is the key of the correct conversion of the quantity of absolute adsorption and excess adsorption. Based on the principle of molecular dynamics and the application of molecular simulation, it simulates the density of supercritical methane under 0 to 50 MPa, and the calculation results are in accordance with National Institute of Standards and Technology (NIST) data. Based on this, combined with the single molecular adsorption theory, it puts forward a new method of conversion of the quantity of absolute adsorption and excess adsorption that can be applied to a great range of pressure. This method has higher accuracy, and breaks through the existing conversion methods with limit of low pressure conditions.

Keywords: Shale gas, density of adsorbed phase, molecular simulation, absolute adsorption.

1. INTRODUCTION

Adsorption capacity is an important component of shale gas reserves. From the publicly available data, we can know that about half of the reserves of shale gas in China are adsorption capacity. The correct evaluation of shale gas reserves is the basis for making the development program correctly. Under the condition of shale gas reservoir, the adsorption of shale-methane belongs to supercritical adsorption. When the adsorption capacity of shale gas was evaluated by adsorption experiments, the isotherm adsorption curve has the characteristics of decreasing after the appearance of extreme point. This phenomenon cannot be explained directly by classical adsorption theory [1] based on absolute adsorption capacity.

In order to explain the characteristic of ultra supercritical isothermal adsorption curve reasonably. Some researchers have improved the classical Langmuir adsorption theory [2-4], but it only limited in the range of pressure from 0 to 12MPa. Dubinin and other former Soviet scholars formed Polanyi-Dubinin adsorption theory [5] on the basis of perfecting Polanyi adsorption potential theory. Sheng Mao and Li Gensheng [6] proposed a more suitable model to

characterize the ultra supercritical adsorption of shale gas. Although the two methods can be used to fit the isotherm supercritical adsorption curve, and the fitting result is well, but the model parameters are lack of physical meaning, can not reflect adsorption mechanism. The method of linearization of isotherm adsorption was proposed without any hypothesis by Zhou Li and Zhou Yaping [7]. Limit pressure is defined instead of saturated vapor pressure, obtained a method for describing supercritical adsorption capacity, Li M [8]. Based on the work of Ozawa *et al*, and Dubinin [9], calculated the adsorption phase density in supercritical state based on experimental data [10]. Based on lattice theory proposed by Ono and Kondo. Xiong Jian [11] transformed the excess adsorption into absolute adsorption by the SRK equation under 0-12MPa, and which is fitted by the improved DA equation.

In summary, the present method and theory for translating the excess adsorption to absolute adsorption based on supercritical adsorption, but the large pressure range and the adsorption theory cannot be considered simultaneously. This paper is based on classical molecular dynamics theory and method, firstly simulated the bulk density of supercritical methane under 0-50Mpa, and calculated the density distribution of methane under different conditions. The calculated results are consistent with the data of NIST, and the excess adsorption was converted to absolute adsorption based on monolayer adsorption theory [6, 12, 13]. The practical adsorption isotherms of shale gas are

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calculated by this method, and the calculation results are of high accuracy, which overcomes the inadaptability of gas equation of state at high pressure and the limitation of regression method.

2. SUPERCRITICAL METHANE ADSORPTION BELONGS TO MONOLAYER ADSORPTION

The equation of state of monolayer adsorption was deduced by Langmuir [14] in 1916, which was first obtained by kinetic method. The Langmuir equation derived from dynamics, and it let us feel that which is related to the mechanism of adsorption and desorption. It assumes that the rate of adsorption v_a is equal to desorption v_d , but it is not truth. Different from the kinetic deduction, the Langmuir equation deduced from statistical thermodynamics can better reflect the equilibrium state of gas-solid adsorption.

The Langmuir equation as equation (1), has a more explicit physical meaning.

$$V = \frac{abP}{1+bP} \quad (1)$$

In the formula: V -Adsorption capacity, cm^3/g ; P -equilibrium pressure, MPa; a -Maximum adsorption capacity, cm^3/g ; b -Langmuir constant, Dimensionless.

The supercritical adsorption of methane refers to the adsorption behavior of methane above the critical condition on the solid surface. Under the condition of original reservoir pressure and formation temperature, methane is always in supercritical state. The boiling point of methane is -161.4°C and the critical temperature is -82.55°C under normal pressure. The shale gas in china is generally buried at 2000-4000m, and the formation temperature is over 40°C , pressure is above 25MPa. The methane is the supercritical state in the reservoir and the adsorption belongs to single molecule layer adsorption, this point has been proved by theory and experiment, and there are two strong evidences.

2.1. The Supercritical Isotherm Adsorption of Methane is Single

The shape of the isotherm adsorption curve is determined by the intrinsic adsorption mechanism, and the type of which can judge some nature of adsorbent surface and interaction of adsorbent with adsorbate. Although the monolayer isotherm monolayer adsorption are in the form of formula (1) and figure 1, But there are many multilayer molecules adsorption that adsorbents containing only 2~3nm micropore, which also have the

form described in formula (1) and figure 1. However, it is impossible to occurring multilayer adsorption [15] above critical temperature, so the single isotherm curve reflects the single adsorption mechanism. No matter how different the combination of solid adsorbent and gas adsorbate is, only one type of supercritical isothermal adsorption curve [16] is observed at present.

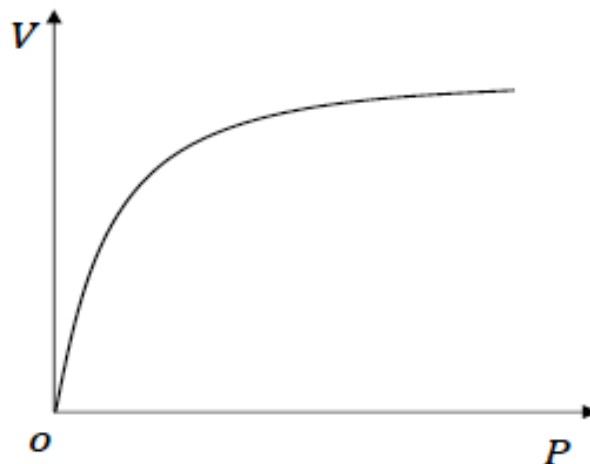


Figure 1: The adsorption isotherm curve of Langmuir.

2.2. The Linear Relationship between Supercritical Adsorption of Methane and Specific Area

The characterization of specific surface of microporous and mesoporous materials plays an important role in studying their properties and broad their uses. Activated carbon *et al*, Carbon materials and other micropore mesopore materials have been applied to a large number of studies related to adsorption. Fu Guoqi [17] found that there has a good linear relationship between adsorption capacity of activated carbon to methane and specific surface area of carbon. The relationship between the adsorption capacity of hydrogen and specific surface area in three kinds of micro-mesoporous materials at 77K are found by Nijkamp [18] through Experiment, the results showed that the adsorption capacity increases linearly with the increase of specific surface area. The adsorption curves of hydrogen isotopes on 21 adsorbents with different porosities and material were determined by Chu XZ [19]. The adsorption capacity was linear with the specific surface area. Xue GW [20] found adsorption capacity of carbon dioxide on silica materials with mesoporous in proportion to specific area. Similar to shale, the same laws are found in coal seam. The more complex composition of organic matter and clay mineral of shale, adsorption capacity

and the specific surface area showed the same positive correlation trend [21].

The relationships between adsorption capacity and specific surface area of gas on micro- mesoporous materials is a strong evidence for methane to single molecule above critical temperature.

3. PHASE DENSITY OF METHANE AND MOLECULAR DYNAMICS SIMULATION MODEL

3.1. Relationship between Bulk Density and Absolute Adsorption Capacity of Gas

Gibbs defined adsorption capacity as the excess adsorption [22] of adsorbed phase beyond the density of bulk phase:

$$n = v_a(\rho_a - \rho_g) \quad (2)$$

In the formula: n -the excess adsorption; v_a -adsorbed phase volume; ρ_a and ρ_g are adsorbed phase density and gas bulk density respectively.

The adsorption phase density ρ_a is calculated by the total amount of adsorbate molecules in the adsorption phase, so the equation (2) can also be transformed into equation (3).

$$n = n_t - v_a\rho_g \quad (3)$$

In the formula, n_t is absolute adsorption capacity, and the difference between n and n_t must be taken into account when evaluating the adsorption capacity

under high pressure. Therefore, obtaining the gas bulk density ρ_g of gas under the large pressure range is the key to the conversion of excess adsorption to absolute adsorption. This paper used the molecular dynamics simulate of methane phase density ρ_g under high pressure range, which can realize the conversion of absolute adsorption.

3.2. Molecular Dynamics Simulation Model and Method

3.2.1. Construction and Optimization of Methane System

Firstly, introduced the methane configuration in the Materials Studio package, and the modeling method is the same as that of Zhong Yonglin [15] in the study of the properties of the properties of supercritical carbon dioxide fluid. Constructed 100 Methane molecules by amorphous cell module, temperature setting 298K, the periodicity three-dimensional structure, finally used the discover module, used the conjugate gradient method to minimize energy, obtained the 100 methane molecules stable structures, As shown in figure 2, crystal cell size is $13.8611\text{\AA} \times 13.8611\text{\AA} \times 13.8611\text{\AA}$.

3.2.2. Simulation Method

The simulation of 0-50MPa was carried out for the established methane system, and the temperature was set to 313k, 333k and 353k. Using Forcite molecular dynamics module, using compass force field, Electrostatic and Van Der Waals using Atom Based sum formula, select the cut-off radius of 12.5a, Anderson Algorithm is used to control temperature and

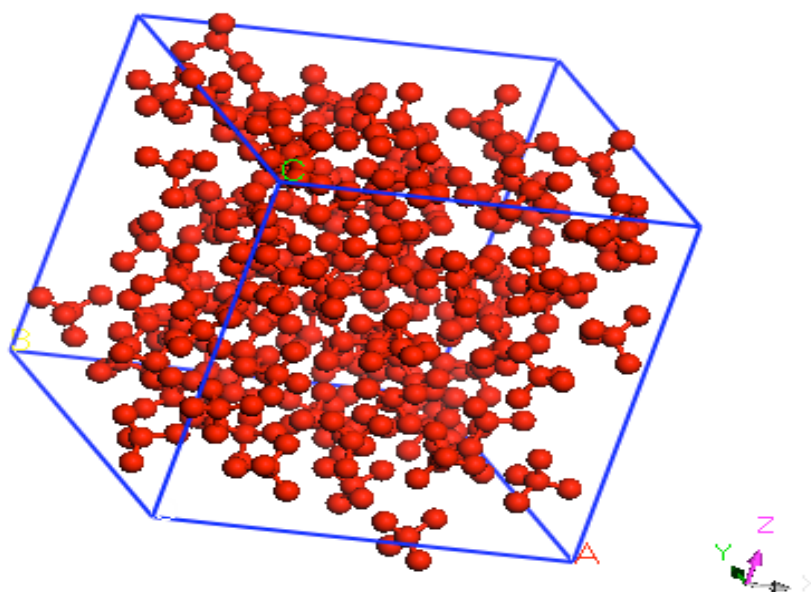


Figure 2: 100 methane molecular periodic configurations.

pressure, the integral step is 1fs, 200ps of molecular dynamics simulation was used to this system under constant temperature and pressure (NPT). The density of the system and the micro configuration of Methane molecule under different temperature and pressure are simulated.

4. CONVERSION OF MOLECULAR SIMULATION RESULTS AND ABSOLUTE ADSORPTION CAPACITY

4.1. Calculation and Comparison of Density

Density ρ is one of the most important physical properties of supercritical methane, which is calculated by the following equation:

$$\rho = \frac{NM}{\langle V \rangle} \quad (4)$$

In the formula, N -the molecular number of methane; M - the molecular weight of methane; V - the volume of analog box; $\langle V \rangle$ - average volume of NPT system.

Figure 3 show out the value of molecules simulation and NIST data under different temperature and pressure, it can be seen that the density of supercritical methane increases with pressure at a given temperature; which decreases with increasing temperature at a given pressure, have sensitivity of pressure and temperature. Under the general shale reservoir conditions (35MPa and 353K), the density of supercritical methane fluid is 0.18g/cm^3 , and there is a big gap between the density of methane liquid (0.426g/cm^3).

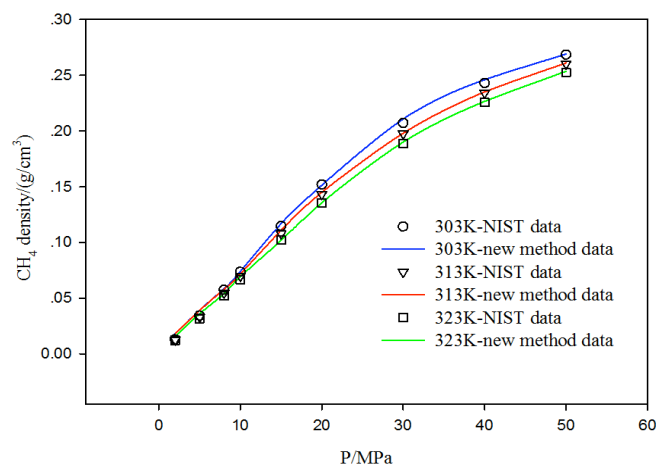


Figure 3: Bulk phase density of supercritical methane.

4.2. Fluid Distribution of Supercritical Methane

Figure 4-A and Figure 4-B are the microscopic configuration of supercritical methane $T = 353\text{K}$, $P = 5\text{MPa}$, $\rho = 0.03\text{g/cm}^3$ and $T = 313\text{K}$, $P = 50\text{MPa}$, $\rho = 0.260\text{g/cm}^3$, we can see that, there is obvious density fluctuation in supercritical methane molecule, that is, local aggregation phenomenon, low pressure formed some aggregates (region b of Figure 4-A), in some place the intermolecular distance (region b of Figure 4-A) fluctuation phenomenon is very obvious; the molecular arrangement tight under high pressure (region d of Figure 4-B), which is not obvious, but there are still some free volume(region c of Figure 4-B).

4.3. Absolute Adsorption Capacity Conversion

Formula (3) shows the excess adsorption transform into the absolute adsorption which has

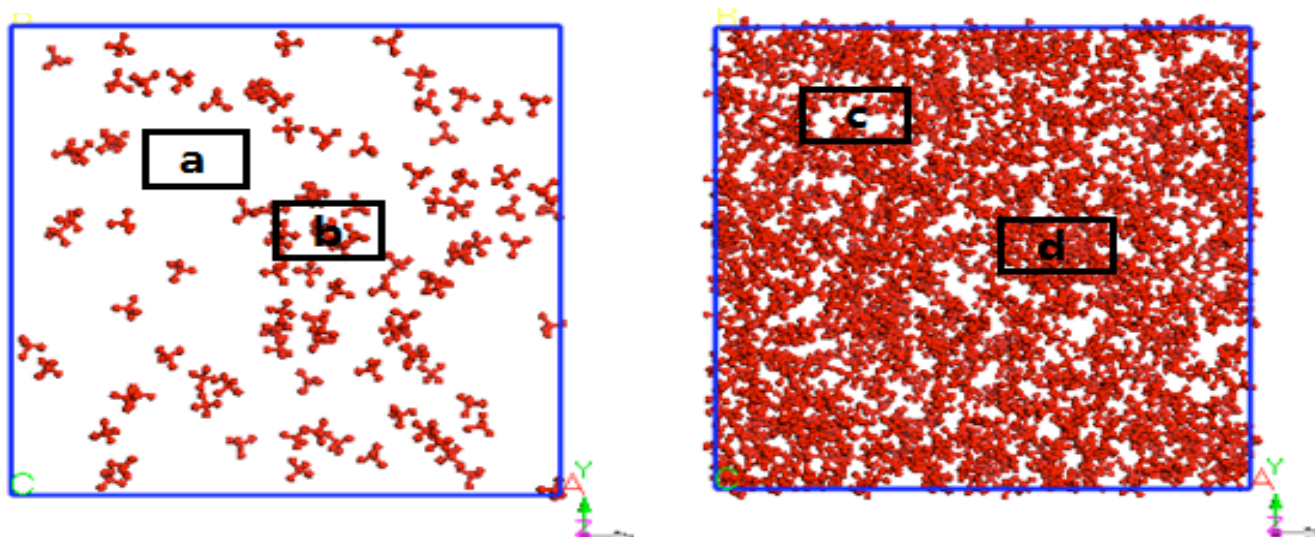


Figure 4: Supercritical methane system configuration diagram.

practical significance should determine the adsorption phase volume and bulk density, the density of adsorbed phase and methane fluid can be calculated by molecular simulation of supercritical methane density, based on the adsorption of methane is supercritical adsorption, adsorption form as a single molecular layer, so the adsorbed phase volume is equal to the product of the specific surface area and the adsorbed thickness of monolayer, as shown in formula (5). The specific surface area data from shale pore analysis data in southern Sichuan Longma creek group, which is $20\text{m}^2/\text{g}$ [23].

$$v_a = Sh \tag{5}$$

In the formula, S -specific surface area, m^2/g ; h -thickness of adsorbed layer, m. Formula 5 is brought into formula 3, the absolute adsorption capacity n_t can be expressed as:

$$n_t = n + Sh\rho_g \tag{6}$$

The experimental data of shale isothermal adsorption comes from the fifth session of the Chinese petroleum engineering design contest, shale samples from southern Sichuan longma creek group shale layers, sampling depth is about 2500m, at present, most of the shale gas experiments refer to the experimental standard of coalbed methane adsorption/desorption, the temperature is 303K, and the adsorption data is shown in Figure 5.

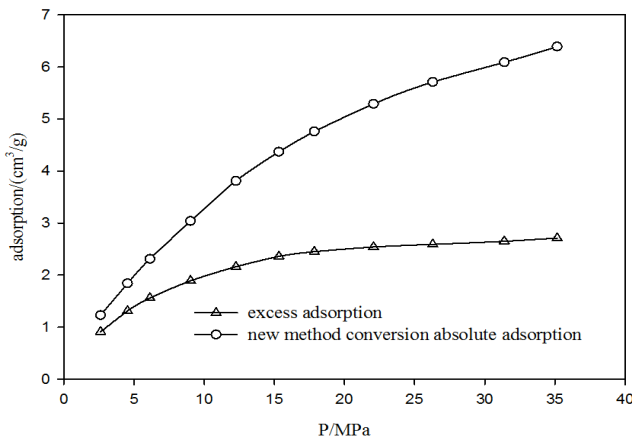


Figure 5: Isotherm adsorption curve and conversion curve for The Fifth China Petroleum Engineering Design Competition.

The conversion of excess adsorption to absolute adsorption was carried by the method in this paper, the result of bulk density by molecular simulation under the different conditions are given, make sure the adsorbed phase volume with supercritical monolayer molecule

adsorption theory and southern Sichuan shale pore analysis data [17]. The isotherms adsorption are shown in Figure 5.

It can be seen from Figure 5 that under the supercritical pressure (4.59MPa) of methane, the excess adsorption and the absolute adsorption have little difference, and which increases gradually with the increase of pressure. It can be seen that the difference between excess adsorption and absolute adsorption has reached more than 150% under the methane reservoir pressure, and which can not be replaced by experimental data in the actual reserves evaluation.

4.4. Comparative Analysis of Transformation Results

Based on experimental isotherm adsorption curve of shale of literature [13], as shown as Figure 6, which under 303K, 313K and 323K. The method in this paper was used to translate the relative adsorption in picture 5 to absolute adsorption, at the same time contrast the conversion results by SKR regression equation in literature [13], the results are shown in Figure 7.

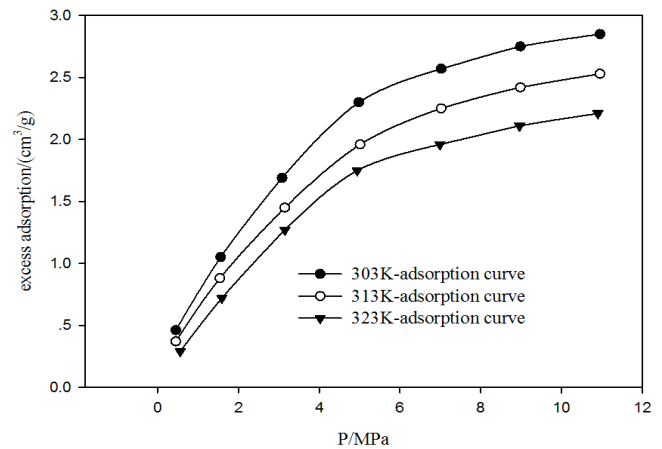


Figure 6: Shale gas adsorption isotherms in literature [13].

It can be seen from Figure 7, compared with the traditional SKR equation regression method based on the equation of gas state calculation, the absolute adsorption translate by the method in this paper is consistent with which by SKR in low voltage stage (0-7MPa), however it begin deviation in high pressure stage, and with the increase of pressure the deviation will be increased.

The author thinks the reason is the inadaptability of gas equation of state under high pressure. Therefore, the method in this paper is stronger, which based on

the analysis kinetic theory, effectively overcomes the limitation of gas state equation in high-pressure inadaptability and regression method.

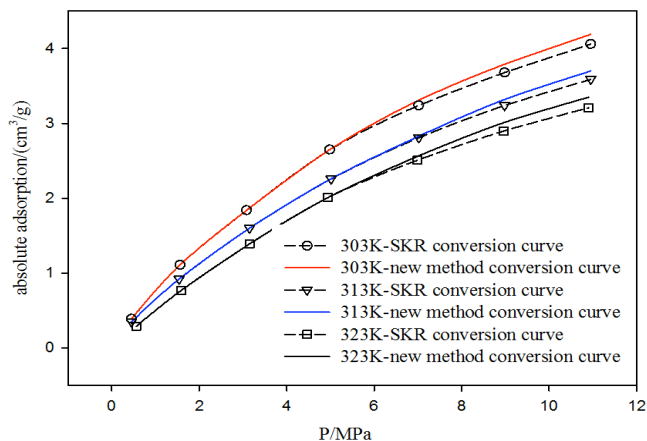


Figure 7: Comparison of transformation results from different methods.

CONCLUSION

Based on molecular dynamics simulation, the methane density distribution under different conditions is obtained by simulating the supercritical methane system. The calculated results are consistent with the data from the National Bureau of standards, which can effectively evaluate the gas phase density of shale gas adsorption.

Using the gas bulk density got by molecular simulations and basing on single molecule adsorption theory, we can translate the excess adsorption measured into absolute adsorption. From the perspective of molecular dynamics, solves the problem that the application of existing adsorption theory to describe the decrease after it reach maximum of isotherm adsorption curve of the supercritical adsorption.

Compared conversion result of absolute adsorption with the conversion method used in this paper and SRK equation regression method which is extensive use, which is supercritical isotherm adsorption curve with the same sample. They are consistent under low pressure (0-7MPa), and show differences which increase with pressure under high pressure. The reason is that the transformation method proposed in this paper, which overcomes the limitation of the SRK method caused by inadaptability of gas equation of state under high pressure, which will expand the absolute adsorption to a large pressure range.

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