Quantum Physisorption of Methane and Carbon Dioxide within Nanoporous Materials

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Abstract: Although numerous investigations reveal the gas physisorption characteristics of porous materials and a variety of theories have also established to describe gas physisorption during the past century, the essence of physisorption behavior of gas within nanoscale space is still indistinct. We find that the physisorption behavior of complex molecular system of methane and carbon dioxide within nanoporous materials exhibits a quantum effect. Inside nanoscale space, potential energy field of gas molecules is a quantized distribution and composes $n+1$ ($n \geq 2$) energy levels located in different orbitals. The lowest potential energy appears near the internal pore surface, where is regarded as ground state (orbital $i = 0$). There are two states for the kinetic energy of molecules, that is, free molecules distributing in orbitals of $i = 1 \sim n-1$ have the same kinetic energy; while adsorbed molecules locating in the orbital of $i = 0$ have the kinetic energy less than that of free molecules. Gas molecules in different orbitals therefore have separate energy levels. Physisorption is exactly the result of energy level transition of molecules in the orbital of $i = 1 \sim n-1$ onto the orbital of $i = 0$. Based on this quantum effect, we established a physisorption equation from the perspective of quantum mechanics to re-understand the basic principles of gas physisorption within nanopores. Energy level transition triggers gas physisorption, and non-uniform spatial distribution of energy-
quantized molecules within nanopores dominates the gas physisorption behavior. The spatial distribution of gas molecules can be adjusted by temperature, pressure and potential energy field. This result contributes to understand and predict the physisorption behavior of CH₄ and CO₂ within nanoporous materials.

1. Introduction

Climate change induced by increasing emission of greenhouse gases of methane (CH₄) and carbon dioxide (CO₂) threaten the living environment of human beings. To reduce carbon emissions, carbon capture and storage (CCS) has long been concerned by global scholars and government organization. Physical adsorption is one of significant properties utilized to accomplish the CCS by nanoporous materials. There are two kinds of storage materials that have received widespread attention, and they are: (a) naturally formed organic-rich rocks (coal, shale), which are rich in nanoscale pores and are an important geological place for CH₄ and CO₂ storage; (b) artificially synthesized nanoporous materials such as metal-organic frameworks (MOFs), which have been widely used to the separation and storage of CH₄ and CO₂ due to their super adsorption capacity and highly adsorptive selectivity.

During the past century, nature of the gas physisorption have been investigated by variously possible theories, such as monolayer adsorption, multi-molecular layer adsorption, potential theory, and volume filling of micropores. Most famous adsorption theory from by Langmuir regards the gas physisorption behavior as the dynamic equilibrium of evaporation-condensation of gas on the plane surfaces. Albeit it has been successfully applied to characterize the physisorption behavior of CO₂ and CH₄, essential issues involving how does gas physisorption trigger within nanoscale pores and what dominates the gas physisorption behavior, are still thought provoking. In
In this study, we proposed a new mechanism from the perspective of quantum mechanics improving to understand the basic principles of physisorption of gases within nanoscale space, and provided a new idea to predict the physisorption behavior of CH₄ and CO₂ within nanoporous materials. In the fields of energy and environment, including geo-resources (coalbed methane, shale gas) assessment and extraction, gas separation and purification, and CCS technique, quantum physisorption theory proposed here would be demonstrated as a powerful tool.

2. Quantum effect of gas physisorption

We proposed a conceptually physical model of quantum physisorption for CH₄ and CO₂ gases. Gas molecules within the confined nanoscale space make up the Boltzmann system, which is characterized by the same molecular properties, negligible intermolecular interaction, and discrete energy levels with an unlimited number of molecules at each energy level. The molecular energy of the Boltzmann system is quantized, that is, the energy levels are separated, which is manifested as a quantum effect. This quantum effect embodies in two aspects: (a) The potential energy of interaction between pore surface and molecule shows a discontinuously quantized distribution, and the spatial potential energy field consists of (n+1) energy levels in different orbitals with a number set of $M=\{i|i \in N, i \leq n, n \geq 2\}$ (Fig. 1A). The potential energy in different orbital is an integer multiple of the smallest potential energy unit $E_\theta$, that is, $E_{pi} = (i-n)E_\theta$, and the lowest potential energy $-nE_\theta$ occurs near the pore surface (Figs. 1B and 1C). (b) The kinetic energy of molecules is simplified to two states according to phase difference, in which the non-adsorbed molecules have the same kinetic energy, that is $E_{vi} = \frac{E_v}{i}, i \geq 1$; while the adsorbed molecule locates in the orbital with the lowest potential energy, and its kinetic energy is $E_{v0} = E_v0, i = 0$. Therefore, gas molecules in different orbitals have separate energy levels, i.e., $E_i = E_{vi} + E_{pi}$. The width of excited molecular orbital
should be an integer multiple of the de Broglie wavelength, which satisfies the condition of maintaining standing wave. Molecules can exist stably in the orbital when this condition is met (Fig. 1D). Based on this understanding, the maximum quantum number \( n \) can be discriminated by a function of considering the gas type, molecular kinetic diameter, and temperature of molecular system, expressed as

\[
n = \frac{d\sqrt{2RTM}}{hNA^{\sqrt{\pi}}} \quad \text{(see Appendix A)}
\]

It can be further expressed as \( n = 0.277\sqrt{T} \) and \( n = 0.399\sqrt{T} \) for \( \text{CH}_4 \) and \( \text{CO}_2 \), respectively. Because the value of \( n \) should be a positive integer, the smaller integer is assigned to the value of \( n \) when the calculated \( n \) value is between two integers.

Theoretically, the maximum quantum number of \( \text{CH}_4 \) and \( \text{CO}_2 \) gradually increase with the increasing temperature. Under the same temperature condition, the maximum quantum number of \( \text{CO}_2 \) is greater than that of \( \text{CH}_4 \).

After molecules are injected into the nanoscale space, it cannot be predicted that the specific location of molecules at the initial moment before the molecules are adsorbed. But in the quantized energy field, gas molecules will be distributed in orbitals \((1 \leq i \leq n)\) by a certain probability distribution, and the distribution conforms to the classic Boltzmann distribution law\(^{24}\), that is:

\[
f_i = \frac{\exp\left(-\frac{iE_0}{k_BT}\right)}{\sum_{j=1}^{n}\exp\left(-\frac{jE_0}{k_BT}\right)}
\]

(Figs. 1E and 1F). Molecules in the same orbital have uniform quantum state, and have diverse quantum states in different orbitals. Ideally, from the surface (the lowest potential energy, orbital \( i = 0 \)) to the inside of a pore, the molecular energy level gradually increases. Excited gas molecules in orbitals \( i = 1 \sim n-1 \) are unstable and will spontaneously return to the ground state (orbital \( i = 0 \)) near the pore surface. When the molecule returns to the ground state orbital, it appears to be adsorbed on the pore surface. Therefore, the physisorption behavior of gas molecules is exactly the result of molecular energy level transition, and the amount of adsorption is the number of molecular transitions.

Energy level transition of gas molecule occurs only when the kinetic energy and potential energy
decrease simultaneously, and follows the principles: (a) Only transitions from $i = 1 \sim n-1$ orbitals (excited state) to $i = 0$ orbital (ground state) occur, showing a transition selectivity; (b) It is not that all the molecules in an excited state will undergo energy level transition, but that they have a certain probability of transition, that is, transition is probabilistic; (c) The probability of energy level transition is equal to each other for all molecules due to the exactly identical molecular properties; (d) Molecular transition speed is equal to the average velocity of molecular motion, that is $\bar{v} = 200 \sqrt{\frac{LRT}{\pi M}}$; 
(e) During the molecular transition, energy releases including both the kinetic energy and potential energy and is numerically equal to the difference in energy level, i.e., $\Delta E_{i-0} = E_i - E_0$.

The orbital of $i = n$ belongs to zero potential energy region, and molecules in this orbital are always in a free state because they get rid of the constraints of gas-solid interaction. In addition, desorption is the reverse process of the adsorption and can be regarded as the process of molecules returning to the excited state from the ground state when receiving external energy.
Fig. 1 Conceptually physical model of quantum physisorption for gases of CO$_2$ and CH$_4$ (take $n=6$ for example).

A. Spatial distribution of quantized energy field within nanopore; B. An ideal pattern of energy level transition of molecules, showing a profile in Figure A; C. Energy distribution within a nanopore showing a straight line in Figure B, where blue line indicates kinetic energy and red line indicates potential energy. In Figure D, taking $n=6$ as a case, individual orbital width equals to the de Broglie wavelength of molecule and total width ($2n\lambda$, length of the blue dotted line) equals to molecular kinetic diameter; in larger pores, individual orbital width equals to the integer multiples of de Broglie wavelength of molecule and total width is $2\xi n\lambda$ (length of the blue dotted line). Figure E shows a case of the distribution of 100 molecules following the probability distribution ($T=298$ K, $E_0=10^{-21}$ J) presented in Figure F.
3. Equation of quantum physisorption

Gas physisorption isotherm is parameterized according to the above physical model. Based on the quantum statistical physics, a quantum equation for the CH₄ and CO₂ physisorption within nanoporous materials was established (see Appendix B). The total amount \( n_a \) of gas adsorption is the sum of molecular transition from energy levels of \( i = 1 \) \( \sim \) \( n-1 \), and can be expressed as:

\[
n_a = \sum_{i=1}^{n-1} n_{ai} \tag{1}
\]

Where \( n_{ai} \) is the adsorption amount of gas molecules at \( i \)-th energy level and is equal to the number of transitions of gas molecules at the \( i \)-th energy level, which can be determined by the quantum physisorption equation:

\[
n_{ai} = \frac{n_{mi}p-k_i z}{p}, n_{ai} \geq 0, k_{i+1} > k_i \tag{2}
\]

where,

\[
n_{mi} = \frac{\exp\left(-\frac{i\varepsilon_0}{k_BT}\right)\times n_L}{\sum_{j=1}^{n-1} \exp\left(-\frac{j\varepsilon_0}{k_BT}\right)} \tag{3}
\]

In formula (2), \( k_i \) is the adsorption constant of gas molecules at the \( i \)-th energy level, which reflects the adsorption saturation speed of gas during pressurization process, generally \( k_{i+1} > k_i \). A smaller \( k \) value indicates a faster physisorption saturation. Gases of different energy levels start to undergo transition at varied initial pressures, which are \( p_i = \frac{k_i z}{n_{mi}} \). In other words, the transition occurs when the molecules reach a certain concentration. During the process of gas pressurization, when the pressure \( p \) reaches the initial pressure \( p_i \), the molecules of the \( i \)-th energy level begin to undergo energy level transitions, which conforms to the quantum physisorption equation.

Additionally, the results obtained by widely used the volumetric and gravimetric methods are the Gibbs excess adsorption \( (n_e) \), which is not the actual amount of adsorbed gas \( (n_a) \). When the gas-adsorbed volume cannot be ignored especially at high pressure, they can be converted into each other.
through the density ratio of free gas to adsorbed gas\textsuperscript{25}, which is mathematically expressed as \( n_e = \left( 1 - \frac{\rho_a}{\rho_e} \right) n_a \).

The quantum physisorption theory is applicable to the adsorption processes of CH\textsubscript{4} and CO\textsubscript{2} in a variety of nanoporous materials (Fig. 2). Two MOFs (Cu\textsubscript{3}(BTC)\textsubscript{2}, MOF-2) and two shale rocks were presented here as cases (see Appendix C). MOFs have homogeneous pore structure\textsuperscript{15}, while the shale is a chemically heterogeneous porous rock\textsuperscript{12}. The quantum physisorption equation can predict the adsorption behavior of CH\textsubscript{4} and CO\textsubscript{2} in the above nanoporous materials, and the adsorption of gases with different energy levels is markedly distinct (Figs. 3a-3d). We can see that the contribution to total adsorption amount decreases as molecular energy level increases particularly at the stage of rapid increase in adsorption amount (Figs. 3e-3h). The gap between the contributions of different energy levels is dominated by probability distribution of molecules in different orbitals. As gas adsorption trends to saturation, the gap gradually decreases until it reaches a stability.

Fig. 2 Potential applications of quantum physisorption theory. Dark gray sphere indicates carbon, light gray sphere indicates hydrogen, and red sphere indicates oxygen.
4. Mechanism of gas physisorption

The physisorption behavior of complex molecular systems of CH₄ and CO₂ within nanoporous space is essentially resulted from energy level transition of gas molecules from excited state to ground state. The ground state orbital locates near the internal pore surface, which resemble the elementary
space described by Langmuir\textsuperscript{19}. The maximum adsorption capacity theoretically equals to the total space occupied by the ground state orbital, which positively associates with internal surface area of pores. Vast specific surface area for MOFs may be the main reason that the MOFs have larger adsorption capacity compared to shale rock. Actual adsorption amount of gas closely relates to the pressure, temperature and potential energy field of gas-solid system. Under certain temperature and pressure conditions, excited gas molecules are initially unevenly distributed in the orbitals ($i = 1$~$n$) following the Boltzmann distribution law. Molecular amount of energy level transition is a function of total number of molecules with the same transition probability. Therefore, the amount of gas physisorption gradually increases due to the increase in the total number of molecules in all the orbitals during pressurization process. Change in pressure, however, does not change the probability of molecular transition. In addition, there is an initial pressure at which adsorption occurs, that is, the law of quantum physisorption is followed when a certain number of molecules is reached.

Potential energy of gas-solid interaction decrease or temperature increase will promote a more evenly molecular distribution within nanoscale space (Figs. 3i-3l), which enhances the difficulty of gas physisorption. As an extreme case, the gas molecules evenly distribute inside nanopores and will be non-adsorptive for a gas-solid system without interaction. Temperature not only alters the probability of energy level transition of molecules but also adjusts the probability distribution of molecules in orbitals together with potential energy field. Temperature increase makes more difficult for gas physisorption, and reduces the probability of energy level transition of molecules, which markedly reduces the maximum adsorption amount.

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**Nomenclature:**

- $n_e$ — excess adsorption amount, mol or mol/g
- $n_a$ — actual (absolute) adsorption amount, mol or mol/g
- $\rho_g$ — density of free gas, cm³/g
- $\rho_a$ — density of adsorbed gas, cm³/g
- $T$ — temperature, K
- $p$ — pressure, MPa
- $z$ — gas compressibility factor, dimensionless
- $M$ — molar mass, kg/mol
- $n$ — maximum quantum number, integer
- $i$ — quantum number, integer
- $E_0$ — smallest potential energy unit, J
- $n_{ai}$ — actual (absolute) adsorption amount of molecules with $i$-th energy level, mol or mol/g
- $n_{mi}$ — maximum adsorption amount of molecules of $i$-th energy level, mol or mol/g
- $k_i$ — adsorption coefficient of molecules of $i$-th energy level, mol·MPa or mol·MPa/g
- $n_L$ — maximum adsorption amount, mol or mol/g
- $K_B$ — Boltzmann’s constant, J/K
- $N_A$ — Avogadro’s constant, mol⁻¹
- $h$ — Planck’s constant, J·s
- $d$ — two times total width of all the excited state orbitals in pore, m
\( \xi \) — positive integer ratio of orbital width to molecular de Broglie wavelength, integer

\( \bar{v} \) — average velocity of molecular motion, m/s

\( f_i \) — probability, fraction

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