

Phase Diagram Analysis of Argon Molecular Adsorption in Nanoporous Materials via Monte Carlo Modeling

Opeyemi Akanbi^{1,4*}, Ogunsakin Oluwakunle^{2*}, Akinsanmi Ige^{3,4}, Peace Folarin⁴, Temitope Yussuff⁴, Julius Oledede⁵

¹ Department of Physics and Applied Physics, University of Massachusetts, Lowell, USA

² Department of Geology, Geological Engineering and Petroleum Engineering, Missouri University of Science and Technology, USA

³ Department of Material Science and Engineering, University of Arizona, Tucson, USA

⁴ Department of Pure and Applied Physics, Ladoke Akintola University of Technology, Ogbomosho, Nigeria

⁵ Department of Mechanical Engineering, Federal University of Technology, Akure, Nigeria

Received August 16, 2023; Accepted November 13, 2023

Abstract

Monte Carlo simulation is employed to investigate the adsorption behavior of argon in nanoporous materials with slit-shaped pores. The study focuses on understanding the phase behavior of fluids confined in these materials, which is crucial for various applications such as gas separation, water purification, and drug delivery. The simulations are performed at three temperatures: 65 K, 110 K, and 160 K, with pore widths of 2 nm. Thermodynamic parameters are computed using NIST's REFPROP program, and saturation pressures are determined for each temperature. The simulations analyze the adsorption isotherms, mean adsorption energies, fluctuations, energy distributions, density of adsorbed molecules, and instantaneous configurations to provide insights into the interactions between adsorbate-adsorbate and adsorbate-adsorbent. The results reveal that the adsorption and isotherm characteristics are influenced not only by temperature but also by the energetic strength of the interactions. Bimodal behavior, indicating layering transitions, is prominent at low temperatures but diminishes as the temperature increases and disappears at supercritical conditions. The study highlights the temperature dependency of the adsorption behavior in nanoporous materials and provides valuable insights for material design and optimization in various applications.

Keywords: Adsorption; Monte Carlo modeling; Nanoporous materials; Adsorption Isotherm; Argon.

1. Introduction

Nanoporous materials with slit configurations have garnered extensive attention and research interest due to their potential applications in molecular adsorption processes such as gas separation, storage, water purification, and drug delivery. The properties of these materials crucially rely on the phase behavior of fluids confined within their nanopores, as distinct from bulk phases, owing to spatial confinement and surface interactions within the nanodomain [1-3]. To gain insights into the equilibrium properties of fluids in nanopores, Monte Carlo (MC) simulation is a widely employed technique for adsorption studies. This method efficiently achieves equilibrium by maintaining fixed experimental conditions while allowing the number of molecules in the adsorbed phase to fluctuate [4-5].

This research adopts Monte Carlo (MC) simulation to investigate the adsorption characteristics of argon within smooth-wall slit pores. The study aims to provide a comprehensive understanding of the structural and energetic aspects, including the molecular configuration and interactions between adsorbed atoms (adsorbate-adsorbate) and between argon atoms and the pore wall (adsorbate-adsorbent). By analyzing energy fluctuation, distribution, and the density of adsorbed molecules as a function of the inter-wall distance (Z) at varying pressures,

obtained from the bulk Argon phase diagram, this work seeks to elucidate the adsorption behavior of argon in this confined system.

1.1. Monte Carlo (MC) simulation

The Monte Carlo (MC) simulation technique is widely used in adsorption processes due to its rapid attainment of equilibrium by probing the grand-canonical ensemble. In the grand-canonical Monte Carlo (GCMC) method, the temperature (T), volume (V), and chemical potential (μ) are held constant, while the number of molecules (atoms) in the adsorbed phase fluctuates throughout the simulation [4]. To achieve this, the simulation generates various configurations through displacement, insertion, and deletion steps. The average energy difference (ΔE) between the old and new configurations is calculated, and each state is accepted or rejected based on the Boltzmann-Transition probability. If ΔE is negative, the transition is accepted; otherwise, it is rejected.

2. Methodology

We conducted Grand Canonical Monte Carlo (GCMC) simulations to study the adsorption of argon in smooth, slit-shaped pores with an effective width of 2 nm. The simulations were performed at three different temperatures: 65 K, 110 K, and 160 K. To obtain the necessary thermodynamic parameters, we utilized NIST's REFPROP program and determined the saturation pressure for each temperature. The initial configurations, including the position and orientation of molecules, were set up for the simulations. Each GCMC simulation consisted of 20,000 steps (Monte Carlo steps per atom) and involved insertion, deletion, and displacement transitions. Throughout the simulations, we computed the mean number of adsorbed argon atoms and their fluctuations, as well as the molecular energies, including instantaneous, wall, and total energies. Additionally, we analyzed the structural configurations and positions of the adsorbed molecules within the nanoporous system.

3. Result and discussion

3.1. Adsorption isotherm

An adsorption isotherm presents a graphical representation of the relationship between pressure (bar) and the mean adsorbed argon atoms ($\langle N \rangle$) as depicted in Figure 1. This plot offers valuable insights into the adsorption mechanism and the interactions that occur between adsorbate-adsorbate and adsorbate-adsorbent. In this study, we simulated the adsorption isotherm of argon in a slit nanoporous material ($Z = 2$ nm) at constant temperatures, encompassing a range of pressures up to the saturation point. Specifically, the simulations were conducted at three temperatures: 65 K (ranging from 0 to 0.03 bar), 110 K (ranging from 0 to 5.5 bar), and 160 K (ranging from 0 to 90 bar). The selection of these pressures was based on information obtained from the bulk phase diagram of argon available in the NIST Chemistry webbook.

At low pressure and 65 K, the adsorption of argon was remarkably rapid, as observed in Fig. 1a, displaying a stepwise isotherm. The initial rise in the number of adsorbed argon atoms at very low pressure indicates a rapid formation of the first layer, highlighting the strong affinity of argon for the pore walls. Subsequently, a relaxation phase follows (in a step-like manner) until a pressure of 0.0455 bar is reached, resulting in only a few atoms being adsorbed. Similarly, at 110 K (Fig. 1b), the adsorption isotherm exhibits a stepwise pattern, indicating the completion of the first layer with a mild relaxation at 0.3 bar, followed by a progressive increase in the number of adsorbed atoms.

The adsorption behavior observed at both 65 K and 110 K, involving the formation of the second layer and complete pore filling, can be likened to a layer transition, resembling capillary condensation. However, unlike the meniscus formation typically seen in slit pores, no meniscus is formed in the nanopore under investigation [6-8]. This transition is characterized by a sharp and significant increase in the amount of adsorbed molecules, resembling the behavior

observed in traditional slit pores [9]. The presence of an inflection point in the isotherm suggests that the adsorbate-adsorbate (Ar–Ar) interaction becomes stronger than the adsorbate-adsorbent (Ar–wall) interaction. Consequently, the rapid adsorption observed at 65 K and 110 K, leading to pore filling, is attributed to the prevailing strong argon–argon interactions within the confined space.

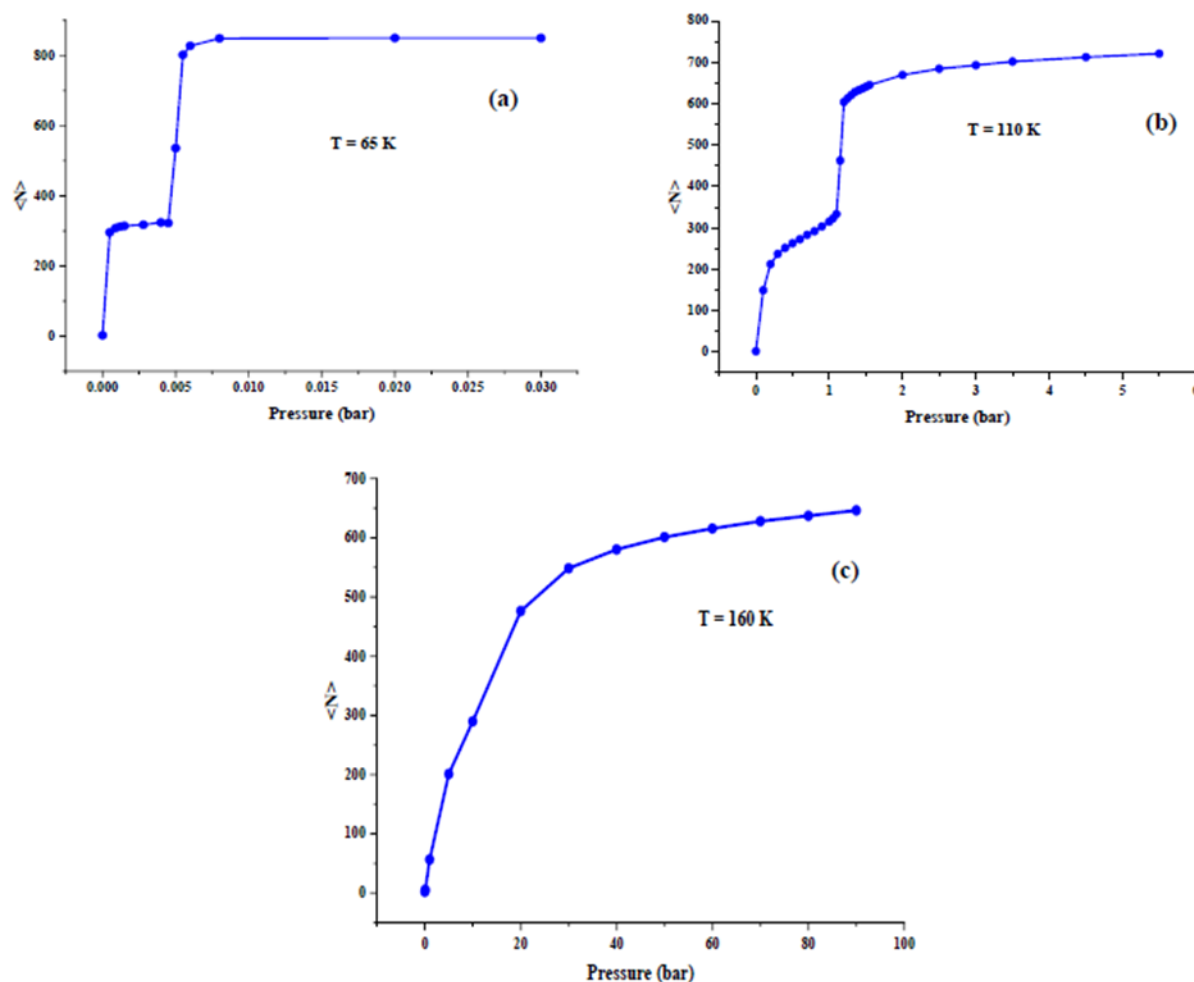


Figure 1. Adsorption isotherms of argon in slit pores were examined at three distinct temperatures: (a) 65K, (b) 110 K, and (c) 160 K.

At higher temperatures (160 K), the adsorption process is characterized by continuous pore filling without evident layer formation (Fig. 3a). This behavior indicates a supercritical adsorption process since the bulk critical temperature of argon is 150.86 K. The isotherms illustrate that the distinct vertical stepwise pattern observed at lower temperatures disappears as the temperature increases. The isotherms evolve from type IV(b) isotherms at subcritical temperatures to type I(b) isotherms at supercritical temperatures, as per the IUPAC classification (Appendix I). Consequently, at higher temperatures, the filling of the nanopore becomes more gradual, and the formation of well-defined layers is no longer observable.

3.2. Mean adsorption energies and fluctuations

The examination of mean energy and the fluctuations in the number of adsorbed atoms, represented by σ_N and σ_E , respectively, offers valuable insights into the adsorption mechanism within split pores. Notably, there exists a strong and significant correlation between the energies and the fluctuation in the number of adsorbed atoms, particularly evident during the layering transition pressure. This observation indicates the importance of understanding the

interplay between energy fluctuations and the dynamic process of adsorption within the confined nanoporous environment.

The significance of $\text{sig } N$ (fluctuation in the number of adsorbed atoms) and $\text{sig } E$ (fluctuation in adsorption energies) becomes crucial during the formation of the second layer and the layering transition, which is akin to capillary condensation. Notably, at low temperatures (60 K and 110 K) and specific pressures (0.005 bar and 1.15 bar), high fluctuation peaks are observed, indicating an unstable adsorbed system just before the new layer formation. This behavior is more pronounced during the layering transition, as reported in previous studies and shown in Fig. 2 (a-b) [7-9]. Conversely, at a higher temperature of 160 K, the fluctuation amplitudes either weaken or become nonexistent, as confirmed by the energy distribution analysis shown in Fig. 2 (c). This suggests that at higher temperatures, the adsorbed system exhibits more stability and a gradual filling without any significant layer formation.

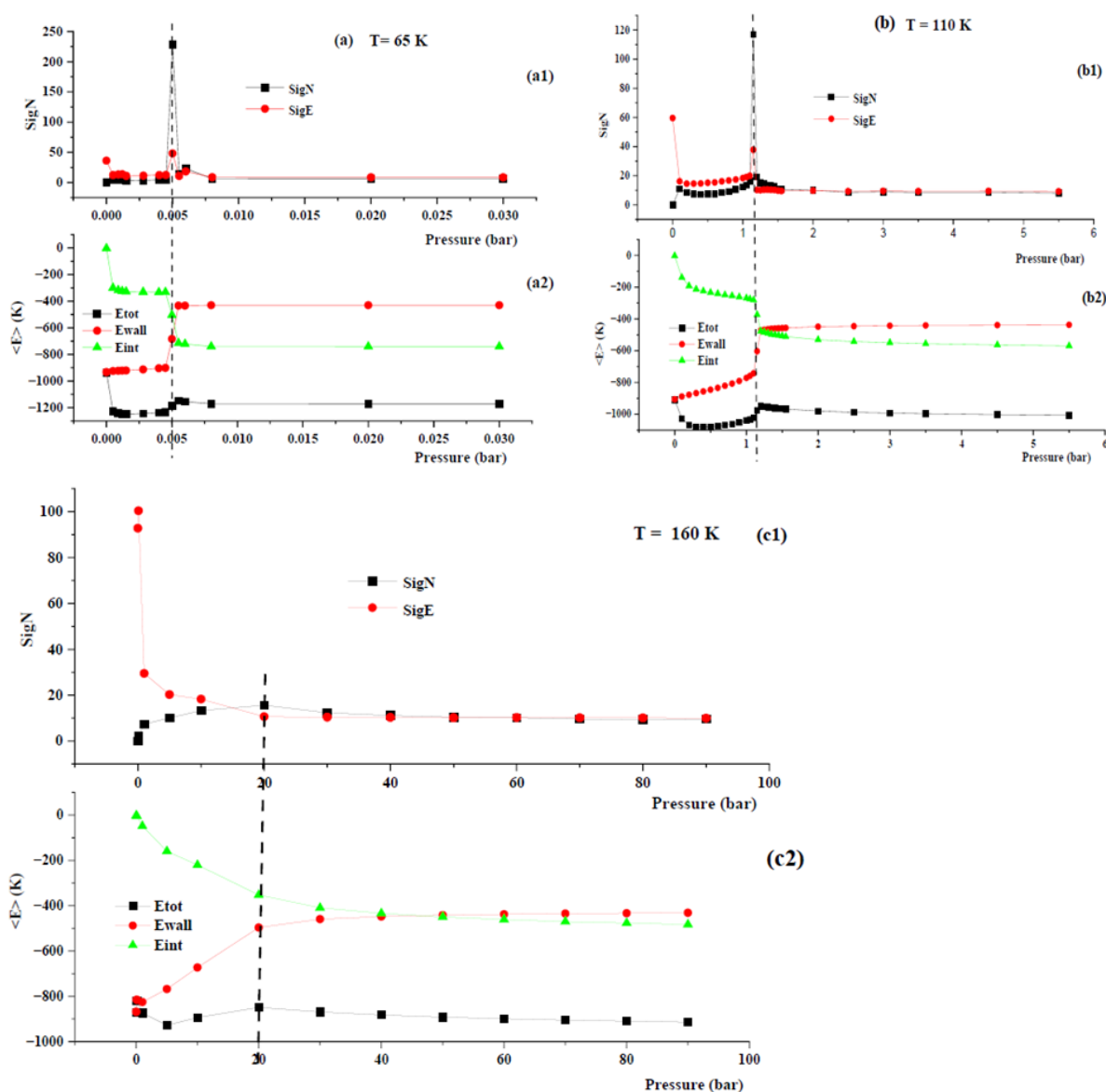


Figure 2. shows the correlations between the mean number of atoms and energy fluctuations (1), as well as the mean energy interaction components (2) (wall, interaction, and total) at three different temperatures: (a) 65 K, (b) 110 K, and (c) 160 K.

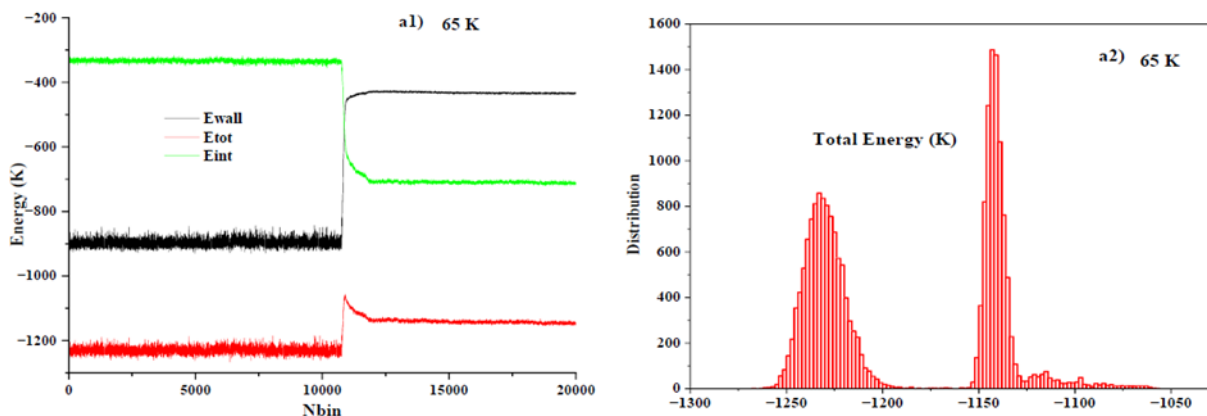
In adsorbed systems, the total energy (E_{tot}) is the sum of the mean intermolecular energy (E_{int}) and the mean wall energy (E_{wall}). At temperatures of 65 K and 110 K, E_{int} rapidly increased and then stabilized, while E_{wall} continuously decreased in response to low pressure fluctuations. This observation supports the isotherm plot, indicating the generation of the first layer due to increased adsorbent-adsorbent interactions. At pressures of 0.005 bar (at 65 K) and 1.15 bar (at 110 K), E_{int} and E_{wall} intersected, demonstrating a significant increase in E_{int} and a decrease in E_{wall} for the interaction energies. This intersection point aligns with a notable spike in energy and fluctuations in the number of adsorbed atoms, visible as a vertical hidden-line in Figure 2. It further confirms the occurrence of an inflection point in the isotherm, suggesting that the adsorbate-adsorbate interaction becomes dominant over the adsorbate-adsorbent interaction at this pressure.

The average adsorption energy, E_{tot} , exhibits an increase upon the formation of the first layer at both 65 K and 110 K temperatures. However, as the adsorption process continues at all three temperatures, E_{tot} shows a gradual decline. This decline can be attributed to the reduced contribution of Ar-wall interactions, particularly noticeable in the second layer. Consequently, the temperature increase plays a significant role in altering the balance between adsorbate-adsorbent and adsorbent-adsorbent interactions, leading to a transition in the adsorption behavior. Moreover, the temperature and the strength of both atom-wall and atom-atom interactions significantly influence the formation of adsorption steps and the process of layering transitions.

3.3. Energy distribution and fluctuation

The examination of the immediate fluctuations in total energy (E_{tot}), wall energy (E_{wall}), and intermolecular energy (E_{int}) offers in-depth insights into the microscopic mechanisms governing the formation and stability of subsequent adsorbate layers. The stability of these layers is influenced by the interplay among various interaction components [10-11]. For this purpose, a simulation involving 20,000 bins was conducted to analyze the energy fluctuations and distributions at pressures corresponding to layering transitions.

The overall energy of adsorption, obtained by summing the fluid-wall and fluid-fluid potential energy in systems with a fixed number of molecules, demonstrates interesting behavior. At 65 K and 0.005 bar, a significant and abrupt decrease in energy fluctuations is observed as the system transitions from one state to another. Furthermore, a bimodal distribution of energy fluctuations provides additional evidence of this transition and layering process. This bimodal behavior indicates the formation of another layer, as the internal energy (E_{int}) increases and the wall energy (E_{wall}) decreases, leading to a stable configuration (see Fig. 3a, points 1-2). Consequently, the filling of additional layers within the pore is accompanied by a slight, discontinuous rise in energy, followed by stabilization.



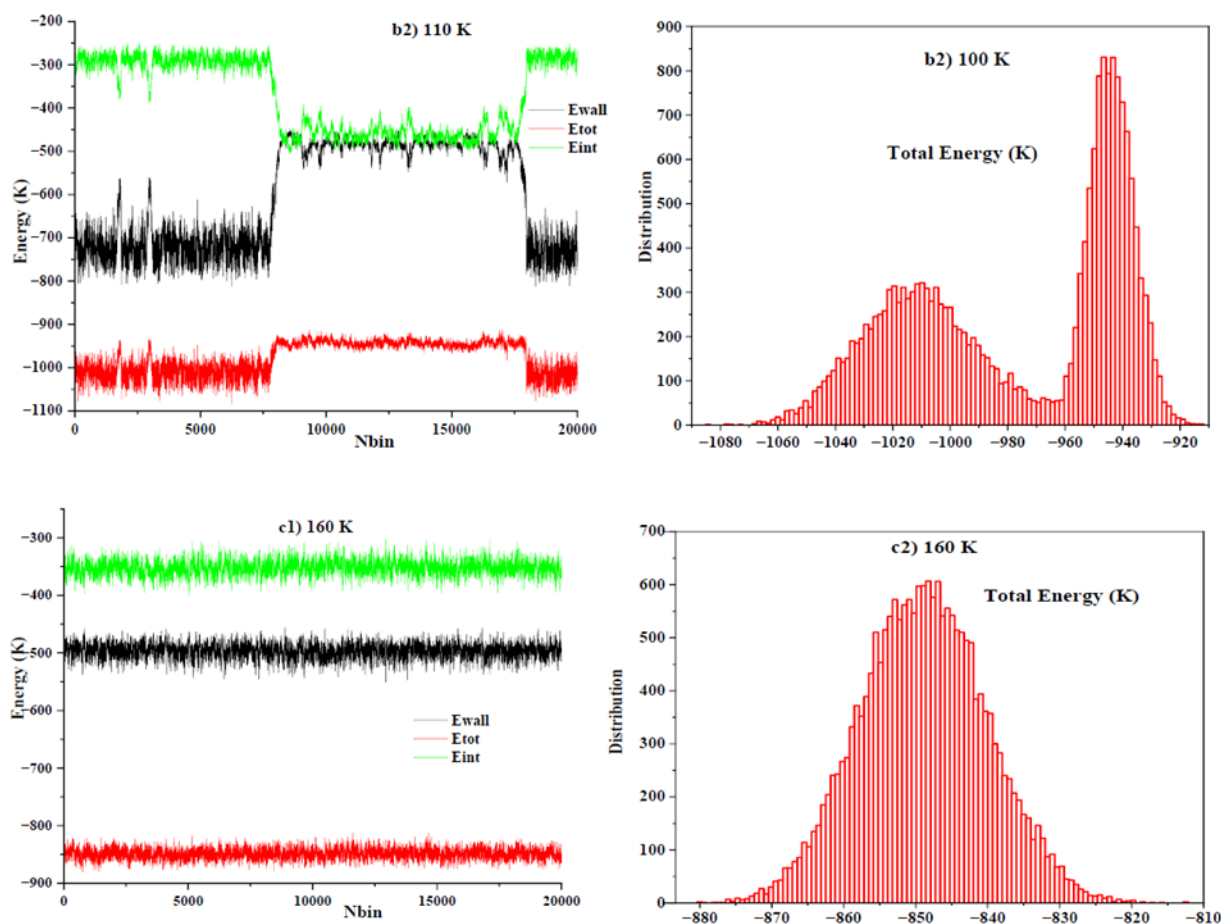


Figure 3. illustrates the energy fluctuations and distributions of argon atoms during the layer transition at a specific pressure. The instantaneous energies (Ewall, Eint, and Etot) are plotted against the simulation steps (Nbin) for three different temperatures (a1, b1, c1). Additionally, the total energy (Etot) distribution is depicted for the energy fluctuations at these temperatures (a2, b2, c2).

At 110 K and 1.15 bar, the energy distribution displayed a bimodal pattern, indicating a potential transition. However, the energy fluctuation analysis revealed that the transition occurred only between approximately 8000 and 18000 bins before returning to its initial state. This suggests that no layer formation occurred during this transition, as the intermolecular energy (Eint) increased while the wall interaction energy (Ewall) decreased. Despite their interaction, no interception was observed, and both energies returned to their initial stable average fluctuation state (Fig. 3, b1). Conversely, at 160 K and 20 bar, no bimodal behavior was observed, and the energy fluctuation remained stable (Fig. 3, c1). This confirms the absence of a layering transition during argon adsorption at 160 K.

Thus, at lower temperatures, the energy fluctuation distribution distinctly exhibits bimodal behavior, indicating structural and phase transformations. Moreover, the time taken for the bimodal shift and state stability during argon adsorption in a slit pore is dependent on the temperature.

3.4. Density of adsorbed molecules

The positions, density, and localization of argon within the 2 nm slit pore were determined at temperatures of 65 K, 110 K, and 160 K, under various pressures. This information was obtained through statistical averaging across the cross section in the Z direction, providing valuable insights into the distribution and concentration of layers formed inside the pore.

At lower temperatures (65 K), the distribution of adsorbed argon in slit pores reveals two distinct, well-defined layers with higher density, indicating the formation of the first layer on both side walls of the pore. These layers indicate stronger interaction forces between the argon atoms and the pore wall. As the pressure increases, the density of adsorbed argon decreases, as illustrated in Figure 4a.

At lower temperatures (65 K), the distribution of adsorbed argon in slit pores reveals two distinct, well-defined layers with higher density, indicating the formation of the first layer on both side walls of the pore. These layers indicate stronger interaction forces between the argon atoms and the pore wall. As the pressure increases, the density of adsorbed argon decreases, as illustrated in Figure 4a.

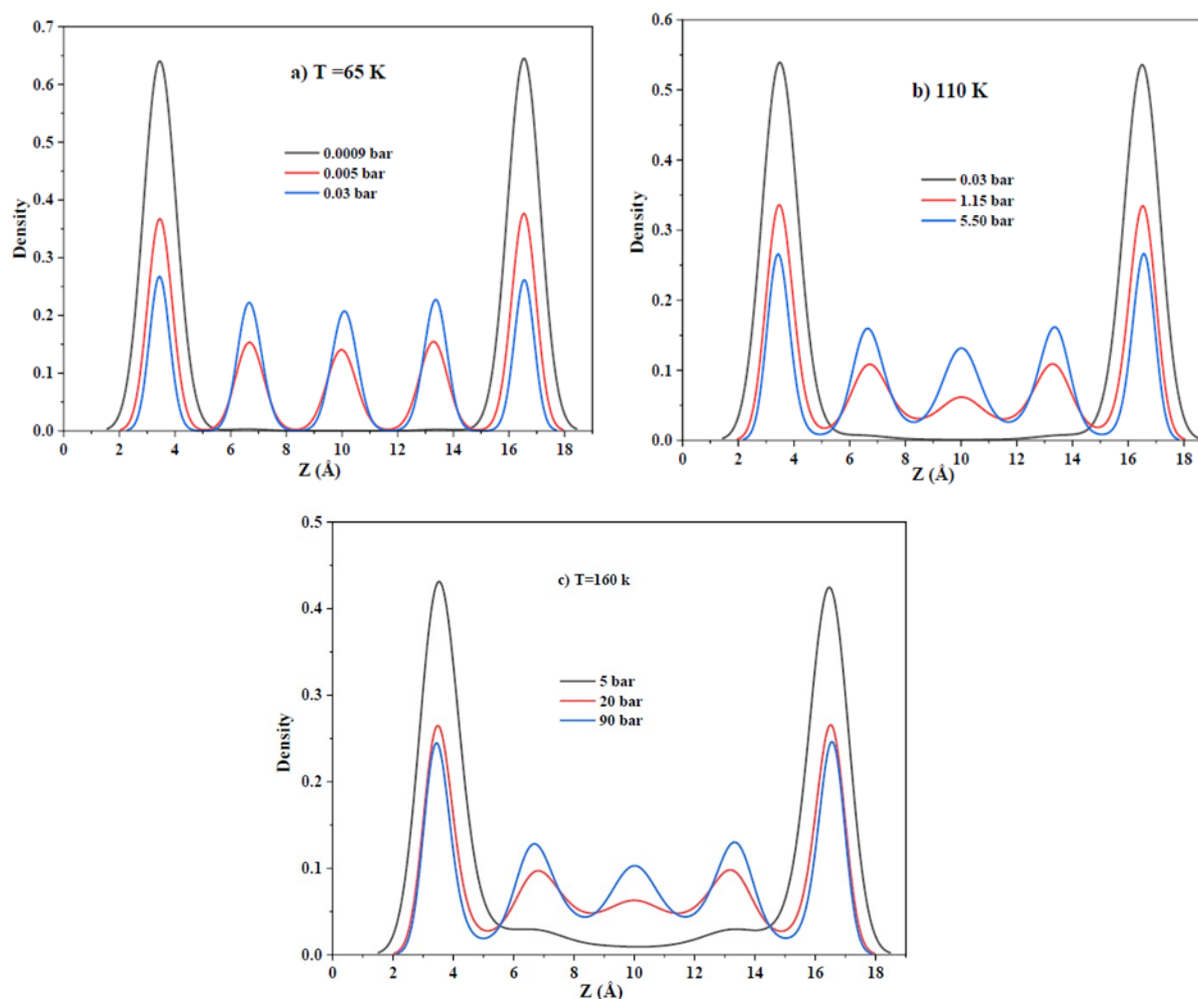


Figure 4. illustrates the distribution of local density for argon adsorbed in slit-shaped pores as a function of distance from the pore wall. The data is shown for four different pressure values.

As the pressure increased, the second and middle layers of argon adsorption were formed in the nanopores. These layers exhibited a reasonably even distribution across the pore walls, but they were less dense compared to the first layer formed at low pressure. Interestingly, at low pressure and higher temperatures (110 K and 160 K), two high-density peaks were observed at the walls of the pores, indicating the formation of the first and second layers. However, the middle layer between these two peaks exhibited a delocalized distribution even at low pressure, indicating a more dispersed arrangement. Nevertheless, as the pressure increased, the second and middle layers became more localized and well-defined within the nanopores. This observation suggests that the interplay between pressure and temperature

plays a crucial role in determining the distribution and localization of adsorbed layers in the nanoporous material.

As a result, the density distribution reveals that at elevated temperatures, especially during supercritical adsorption, the arrangement of adsorbed argon atoms undergoes structural changes, showing distinct differences between low-pressure and high-pressure ordering. This phenomenon could be attributed to the increased compression and densification as pressure and temperature rise within the system. However, the positions of the well-defined layer peaks remain unchanged. Consequently, the density within the simulated slit pores ($Z = 2$ nm) remains constant irrespective of pressure variations, as the locations of the five generated peaks (layers) are independent of both pressure and temperature.

3.5. Instantaneous configurations (structures)

The immediate arrangement of argon atoms adsorbed in a slit pore was examined to characterize the structural aspects during various stages, including the first layer, second layer, complete pore filling, and the layering transition. The analysis compared these configurations at different pressures, considering the mechanisms observed in the isotherms and the mean and instantaneous fluctuations and distributions of interaction energies. The study thoroughly investigated the formation of the first and second layers, complete pore filling, and the occurrence of layering transitions. These observations indicate that the positions of the formed layers remain consistent and are independent of temperature and pressure.

At a temperature of 60 K, a well-packed and organized first layer covers the pore walls in a parallel arrangement. This regular monolayer formation on the pore walls gives rise to a characteristic stepwise isotherm, providing evidence of a strong adsorbate-adsorbent interaction. Once the first layer completely covers the walls, rapid filling of the pore ensues, signifying a distinct and well-defined layer transition, as illustrated in Fig. 5a, sections (1-3).

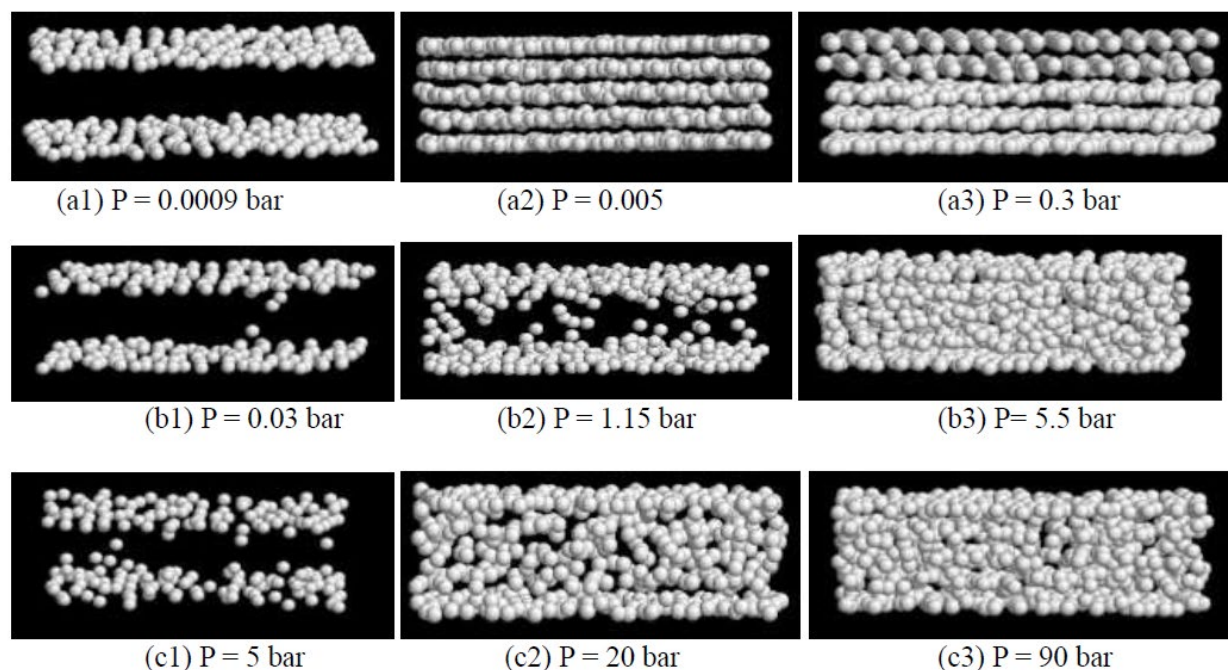


Figure 5. presents instantaneous configurations of argon adsorption in a 2 nm slit pore at different temperatures: (a) 65 K, (b) 110 K, and (c) 160 K.

At a temperature of 110 K (Fig. 5b, 1-3), the formation of the first layer is not clearly defined, similar to the isotherm's less steep shape depicted in Fig. 1b. At a pressure of 1.15 bar, where the mean energy and fluctuations in the number of adsorbed atoms suggest a

layering transition, the situation is different. The argon atoms appear to become sparser in the region away from the pore walls compared to the area close to the pore walls.

At 160 K, the formation of the first layer becomes highly dispersed and lacks clear definition, suggesting a weakening of the wall-atom interaction as the temperature increases. The isotherm at this supercritical temperature exhibits a gradual and continuous increase in the adsorbed argon beyond the first layer. The pore is completely filled, and the system achieves greater stability without distinct layer formation, taking on a liquid-like configuration. Moreover, this observation indicates a distribution of adsorption energies within the system.

Hence, at elevated temperatures, the adsorption mechanism undergoes modification, as evident from the instantaneous configuration analysis. Additionally, the isotherm indicates a transition from Type IV(b) to Type I(b), which signifies a shift in the equilibrium between gas-wall and gas-gas interactions. This transition results in a more gradual filling of the pore due to changes in pressure and energy fluctuations.

3.6. Molecular final energy

The effectiveness of the atom-wall interaction plays a vital role in the adsorption process, influencing various characteristics such as the number of adsorbed atoms, the shape of the isotherm, adsorbate stability, and the pressure at which layering transitions occur. Additionally, this interaction significantly impacts the stability of the adsorbed system, as it competes with other inter-atomic interactions [8]. To analyze the Ar-wall interaction energy (referred to as molecular final energies), the final configuration of adsorbed argon atoms at a distance of two nanopore walls (Z) was considered.

The strength of the interaction between argon atoms and the pore walls increases as the atoms are adsorbed onto the walls, reaching its peak when the first layer is formed. At low temperatures (65 K), the filling of the pores is characterized by a slight, intermittent decrease and subsequent stabilization of the Ar-wall energy, indicating a layering transition akin to capillary condensation. This transition is influenced by factors such as the intensity of atom-atom contact, temperature, and pressure. The configuration at 65 K reveals the complete formation of five layers during the layering transition (Fig. 6a). However, no such layering transition is observed between 110 K and 160 K, as evident from the mean energy and fluctuations in the number of adsorbed atoms (Fig. 6 b-c). The pore is filled in these cases through a consistent interaction between the adsorbate and the pore walls, as well as between adsorbate molecules themselves.

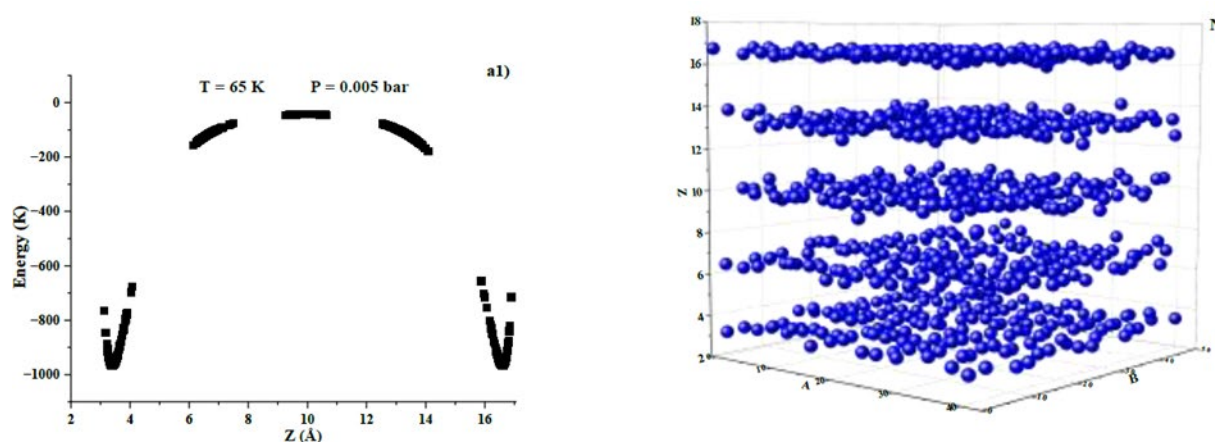


Figure 6. illustrates the pore models representing the interaction energy (E_{wall}) between argon and the pore wall, along with the corresponding final configurations (positions) on the right side, at different temperatures: (a) 65 K.

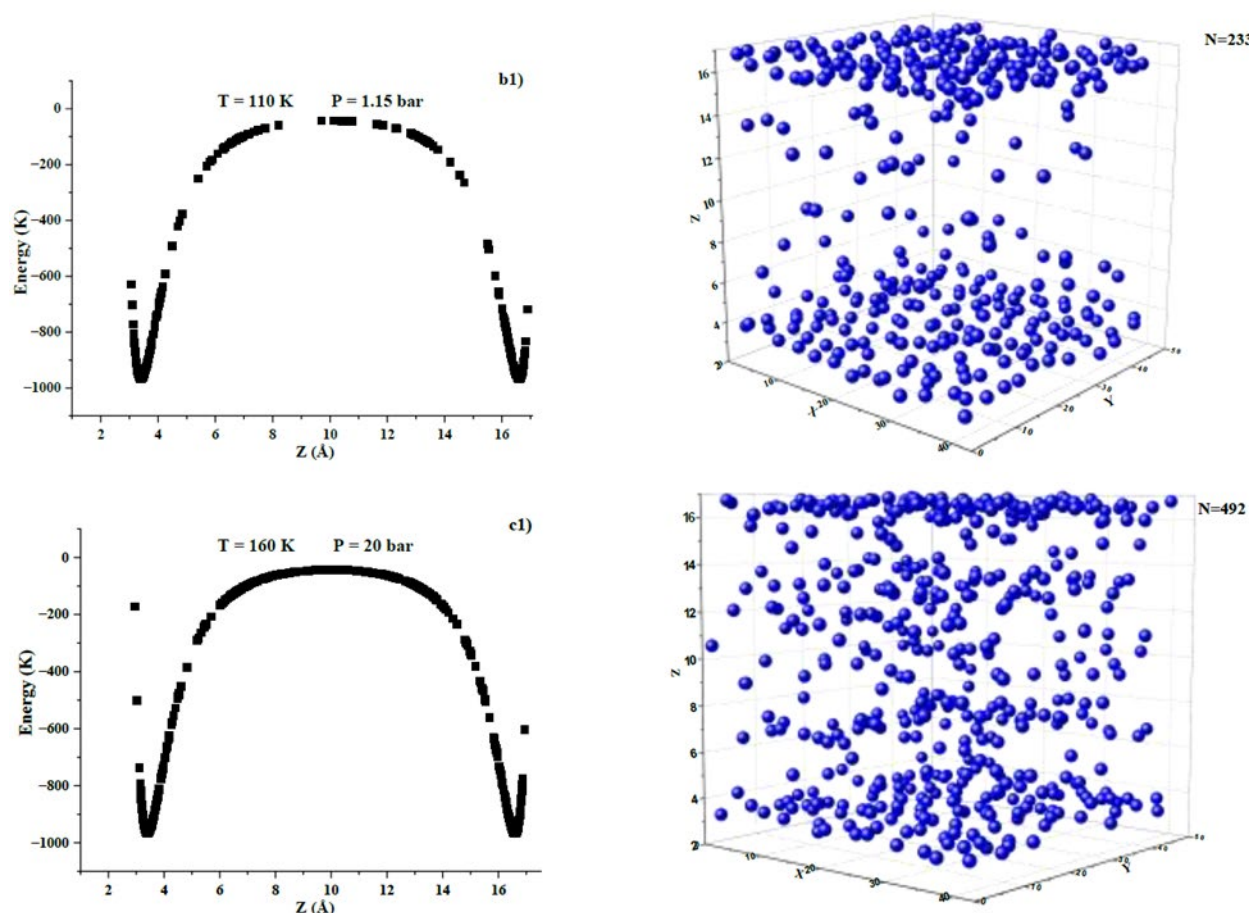


Figure 6. illustrates the pore models representing the interaction energy (E_{wall}) between argon and the pore wall, along with the corresponding final configurations (positions) on the right side, at different temperatures: (b) 110 K, and (c) 160 K.

4. Conclusion

The results obtained from Monte Carlo simulation provide valuable insights into the adsorption behavior of argon in slit nanopores. It was observed that the rapid adsorption and the distinctive steplike shape of the adsorption isotherm in the nanopores are influenced not only by temperature but also by the energetic strength of the interactions between argon atoms (Ar-Ar) and argon atoms with the pore walls (Ar-wall). These interactions compete to stabilize the system during adsorption. As the temperature increases, the adsorption process changes, and the steplike adsorption pattern becomes more gradual and dispersed within the pore, as revealed by the analysis of instantaneous configurations. Additionally, the density and localization of the layers formed in the nanopores are dependent on both temperature and pressure, while their positions remain constant. An interesting observation is the presence of bimodal behavior, particularly at low temperatures, which suggests the occurrence of layering transitions, akin to capillary condensation. This bimodal behavior can be readily observed from the mean and instantaneous fluctuations of the number of adsorbed atoms and the energy fluctuation distribution. However, as the temperature increases, this bimodal characteristic diminishes and eventually disappears entirely at supercritical conditions. At a constant temperature, the occurrence of the layering transition is primarily determined by the relative strength of the Ar-wall atom contact and the interactions between the adsorbed Ar atoms.

Overall, the Monte Carlo simulation offers valuable insights into the complex interplay of temperature, energetic interactions, and adsorption behavior in slit nanopores. These findings

contribute to a deeper understanding of the adsorption process and can aid in the development and optimization of nanoporous materials for various applications in gas separation, water purification, and drug delivery.

References

- [1] Broom DP, Thomas KM. Gas adsorption by nanoporous materials: Future applications and experimental challenges. *MRS Bulletin*. 2013; 38(05): 412–421.
- [2] Zou R., Abdel-Fattah AI, Xu H, Zhao Y, Hickmott DD. Storage and separation applications of nanoporous metal–organic frameworks. *CrystEngComm*. 2010; 12(5): 1337–1353.
- [3] Cárdenas H, Müller E. Molecular Simulation of the Adsorption and Diffusion in Cylindrical Nanopores: Effect of Shape and Fluid–Solid Interactions. *Molecules*. 2019; 24(3), 608.
- [4] Zhang H, Bucior BJ, Snurr RQ. Molecular Modeling of Carbon Dioxide Adsorption in Metal–Organic Frameworks. *Modelling and Simulation in the Science of Micro- and Meso-Porous Materials*, 2018; 99–149.
- [5] McIntyre SM, Shan B, Wang R, Zhong C, Liu J, & Mu B. Monte Carlo Simulations to Examine the Role of Pore Structure on Ambient Air Separation in Metal–Organic Frameworks. *Industrial & Engineering Chemistry Research*, 2018; 57(28), 9240–9253.
- [6] Barsotti E, Tan SP, Saraji S, Piri M., & Chen JH. A review on capillary condensation in nanoporous media: Implications for hydrocarbon recovery from tight reservoirs. *Fuel*, 2016; 184, 344–361.
- [7] Kuchta B, Firlej L, & Maurin G. Mechanism of adsorption in cylindrical nanopores: The roles of fluctuations and correlations in stabilizing the adsorbed phase. *The Journal of Chemical Physics*, 2005; 123(17), 174711.
- [8] Kuchta B, Firlej, L, & Maurin G. Influence of Strength of Atom–Wall Interactions on Adsorption Mechanism. *Adsorption*, 2005; 11(S1), 367–372.
- [9] Jiang S, Rhykerd CL, & Gubbins KE. Layering, freezing transitions, capillary condensation and diffusion of methane in slit carbon pores. *Molecular Physics*, 1993; 79(2), 373–391.
- [10] Coasne B, Gubbins KE, Hung FR., & Jain SK. Adsorption and structure of argon in activated porous carbons. *Molecular Simulation*, 2006; 32(7), 557–566.
- [11] Xu L, Zhang J, Ding J, Liu T, Shi G, Li X, Dang W, Cheng Y, & Guo R. Pore Structure and Fractal Characteristics of Different Shale Lithofacies in the Dalong Formation in the Western Area of the Lower Yangtze Platform. *Minerals*, 2020; 10(1), 72.

To whom correspondence should be addressed: Opeyemi Akanbi, Department of Physics and Applied Physics, University of Massachusetts, Lowell, USA; e-mail: akanbiopeyemisamson@gmail.com