

Review Article

Investigation of the Zeta Adsorption Model and Gas-Solid Adsorption Phase Transition Mechanism Using Statistical Mechanics at Gas-Solid Interfaces

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This review examines the significance of the zeta adsorption model in physics and its integration with statistical mechanics within the field of interface adsorption. Through a comprehensive analysis of existing research, this study presents the collective findings and insights derived from the reviewed literature. The zeta adsorption model, proposed by Ward, has gained recognition for its seamless extension into the thermal disequilibrium region without encountering singularities. By incorporating principles from quantum mechanics and statistical thermodynamics, this model offers fresh perspectives on the adsorption of gas molecules on solid surfaces. Notably, it demonstrates enhanced accuracy in describing the adsorption performance of mesoporous materials and nanomaterial surfaces, surpassing the limitations of traditional models such as the BET isotherm. Additionally, this review explores the behavior of cluster formation under varying temperature and pressure conditions. It highlights the correlation between increasing pressure ratios and the decreased availability of empty adsorption sites, resulting in the formation of larger clusters within the adsorbate. Ultimately, this process leads to a transition from adsorption to condensation, where the liquid phase wets the solid surface. Moreover, the zeta adsorption model provides a solid theoretical foundation for understanding crucial aspects of gas-solid interface adsorption. It enables the determination of the distribution of adsorbate clusters on gas-solid interfaces, facilitates the identification of wetting pressure ratios during phase transitions, and allows for the calculation of solid surface tension under conditions of zero adsorption. Noteworthy parameters such as the bonding strength (β) between the solid surface and adsorbed atoms significantly influence the overall strength of the solid-fluid interaction. Furthermore, the phenomenon of surface subcooling, which necessitates sufficient energy for the transformation from adsorbed vapor to condensate liquid, plays a pivotal role in studying interface phase transitions. Additionally, this review investigates the thermodynamic stability of the adsorbate through an analysis of molar latent heat. It reveals that beyond a critical adsorbate coverage, the formation of critical-sized clusters and the ensuing interactions among these components render the adsorbate unstable. This instability prompts a transition from the interface to a liquid phase, followed by subsequent adsorption onto the surface. In summary, this literature review highlights the significant contributions of the zeta adsorption model to the field of physics, particularly in the context of interface adsorption. It serves as a valuable tool for studying various materials and cluster formation, thanks to its seamless extension into the thermal disequilibrium region and its incorporation of principles from quantum mechanics and statistical thermodynamics. By presenting a synthesis of existing research, this review sheds light on the advantages of the zeta adsorption model and paves the way for further investigations into gas-solid interface adsorption phenomena.

1. Introduction

1.1. Classic Gas-Solid Interface Equilibrium Adsorption Isothermal Models. Adsorption at the gas-solid interface is a prominent research field in surface science and finds

extensive applications across various engineering technologies [1, 2]. It is widely acknowledged as a valuable approach for environmental protection, separation processes, gas purification, gas storage, and other important applications [3–5]. Understanding and studying adsorption at the gas-solid

interface are essential for investigating adsorption mechanisms, evaluating adsorption performance, and developing efficient processes and technologies in these domains. Equilibrium adsorption isotherms at the solid-vapor interface have been investigated thoroughly [6–8].

These models are predominantly derived from the Langmuir [9] adsorption isotherm model. Building upon the Langmuir model, subsequent researchers have proposed numerous classical adsorption models. The Freundlich [10] isotherm represents a pioneering empirical equation that demonstrates applicability not only to gas adsorption on solid surfaces but also to solute adsorption from solutions onto solid surfaces. However, this isotherm fails to effectively correlate experimental data at low pressures. Sips [11] introduced a semiempirical equation, which bears resemblance to the Freundlich isotherm but predicts that the surface coverage tends towards unity at sufficiently high pressures. This equation is commonly referred to as the Langmuir-Freundlich model. Another empirical isotherm, resembling the form of the Toth isotherm [12], finds wide applicability and yields satisfactory results in both low and high-pressure regimes. Based on the assumption in the Langmuir theory that the surface of a solid is homogeneous, the BET [13] theory emerged, which considers adsorption to occur in multiple molecular layers. According to this theory, additional molecules can adsorb onto the previously adsorbed ones, and it is not necessary for the first layer to be completely filled before the second layer begins to form. Moreover, the adsorption process of the first layer differs from that of subsequent layers. The adsorption of the first layer occurs due to the molecular attraction between the adsorbent and the adsorbate, while the adsorption of the second layer and beyond is governed by the intermolecular forces among the adsorbate molecules. As the interacting entities differ, the adsorption enthalpy also varies. The adsorption enthalpy of the second layer and subsequent layers approaches the heat of condensation [14].

For the BET theory, if the relative pressure is too low, it fails to establish the physical adsorption of multiple molecular layers, while if the relative pressure is too high, capillary condensation is likely to occur, leading to inflated results [15]. The two-parameter BET equation, characterized by the parameters C and the monolayer volume V_m , is commonly applicable when the relative pressure (p/p_0) ranges from 0.05 to 0.35 [16]. If the relative pressure is too low, it is insufficient to establish multilayer adsorption. Conversely, when the relative pressure exceeds 0.35, deviations may occur due to significant capillary condensation. In contrast, the three-parameter BET equation, incorporating the additional parameter n (representing the number of molecular layers of gas adsorbed on the solid surface), is suitable for relative pressure values in the range of 0.35 to 0.60. The BET adsorption isotherm specifically applies to multilayer physical adsorption and is commonly employed for determining the specific surface area, pore structure, pore shape, and pore size distribution of solid materials [17–20]. Additionally, the Dubinin-Radushkevich [21] filling theory, based on the Polanyi adsorption theory, applies to micropores where the pore diameter is comparable to the diameter of

the adsorbate molecule. In such micropores, the two opposing pore walls are in close proximity, resulting in an overlap of the potential fields exerted by the pore walls on the adsorbate molecule [22].

These adsorption models are extensively utilized for inferring adsorption mechanisms, evaluating adsorption performance, and determining adsorbent properties such as specific surface area, pore volume, and pore size distribution [23–28].

1.2. Integration of Gas-Solid Adsorption Models into Gibbsian Thermodynamics. For the study of interfacial adsorption characteristics at equilibrium, the first step is often to determine the adsorption isotherm and then to analyze the essence of the adsorption process in combination with the theoretical model of adsorption [29]. An equilibrium adsorption isotherm relation is formulated that predicts an amount adsorbed on the specific surface area at different vapor phase pressures. In the most isotherm formulations, the conception was that adsorption takes place in layers, and the molecules were suggested to adsorb on the first monolayer and then to form a second layer and possibly higher layers. The Gibbs adsorption equations for gas adsorption at the gas-solid interface are based on thermodynamics.

$$d\sigma = -\sum_i \Gamma_i d\mu_i, \quad (1)$$

where σ is the interfacial tension, μ_i is the chemical potential of component i , and Γ is the adsorption amount of component i on the unit interface. For the gas-solid interface, if there is only one adsorbed phase, and its pressure is so low that it can be regarded as an ideal gas,

$$d\mu = RT \ln p. \quad (2)$$

When Eq. (2) is substituted into Eq. (1), we get

$$\Gamma = -\frac{p}{RT} \left(\frac{\partial \sigma}{\partial p} \right). \quad (3)$$

With the help of this formula and the introduction of a suitable physical model of the adsorption layer, the gas-solid adsorption isotherm can be established, which is the basis for studying the adsorption mechanism.

1.3. The “Physically Unrealistic” of Classic Gas-Solid Adsorption Models When $p/p_0 = 1$. In the most isotherm formulations, the conception was that adsorption takes place in layers, and the molecules were suggested to adsorb on the first monolayer and then to form a second layer and possibly higher layers. Although these isotherms are capable of modeling various experimental systems, a challenging aspect of these models is their inability to account for limited surface coverage as pressure approaches infinity [30, 31].

The resulting multiple-BET (Eq. (13)) is

$$V = \sum_1^{\infty} V_n = \frac{V_m c}{(1-x)(c-1)x} \sum_1^{\infty} x^n = \frac{V_m c x^V}{(1-x^V)(1+(c-1)x^V)}, \quad (4)$$

where c is referred to as the BET c -constant, $x = p/p_0$, and p_0 is the saturation vapor pressure.

Here, V is the volume adsorbed, and V_m is the volume corresponding to the first monolayer.

When p approaches p_0 , that is, $x \rightarrow 1, V \rightarrow \infty$, although adsorption in the first layer is strongly favored relative to higher layers, thermodynamically, V is necessarily finite at $x = 1$. This is theoretically impossible for physical adsorption. Furthermore, when the pressure exceeds the saturation vapor pressure, the volume adsorption V is predicted to be negative.

Cassie [32] has published a statistical derivation of the BET equation. However, Cassie did not address the issue of V becoming infinite at the pressure of the adsorbate, $p = p_0$. Anderson [33] pointed out that better agreement with experimental data was obtained if x^V in the BET isotherm expression were multiplied by a constant that was less than unity. The expression becomes

$$\frac{V}{V_m} = \frac{c\alpha x^V}{(1-\alpha x^V)(1+(c-1)\alpha x^V)}, \quad (5)$$

where α is the Anderson parameter and c is referred to as the BET c -constant; when the Anderson correction is introduced, the adsorption is no longer predicted to be infinite as the pressure ratio x^V approaches unity. With this modification of the BET isotherm, Ward provides a multilayer BET expression similar to that of Anderson.

$$n^{sv} = \frac{M c \alpha x^V}{(1-\alpha x^V)[1+(c-1)\alpha x^V]}, \quad (6)$$

where M denotes the number of adsorption sites per unit area of the solid surface. However, there are no isothermal adsorption models that consider the adsorbed gas as clusters of molecules on adsorption sites.

Classical BET equation and modified AD equation are not suitable for analyzing the adsorption phase transition process. When the adsorption equilibrium pressure approaches the saturation pressure, the adsorption amount calculated by the above theoretical calculations always tends to infinity. Under supersaturated conditions, the interfacial adsorption amount is negative [34], which is obviously not in line with physical laws. An adsorption isotherm, namely, zeta isotherm, is developed by approximating the adsorbed vapor as molecular clusters adsorbed at sites. Based on cluster conception, Ward and Wu [35] first proposed the zeta isotherm adsorption theory, which starts from the perspective of statistical thermodynamics [36] and proposes the basic adsorption mode that the adsorbate is adsorbed on the solid surface in the form of clusters.

To investigate the adsorption isotherm from a molecular perspective, it is necessary to introduce the hypotheses of statistical thermodynamics and the ensemble theory.

An ensemble is a collection of a very large number k of systems, each constructed to be a replica on a thermodynamic (macroscopic) level of the actual thermodynamic systems. The ensemble would consist of k systems, all of which are constructed to duplicate the thermodynamic state (N, V , and T) and environment.

Using layer-by-layer BET adsorption isotherms, [37] determined the surface area and attempted to compare the adsorption on different samples of a material by expressing the adsorbed amount per unit area. However, due to the inability of the BET isotherm to describe all equilibrium data, it cannot be used to verify Gibbs' idea that the specific adsorption of a vapor is a property of the substrate and determines the solid surface energy. Furthermore, these studies using the BET surface area resulted in a nonphysical prediction of an infinite adsorption amount when x^V reaches 1. Zeta adsorption model has been successfully used to predict the infinite amount of adsorption at saturation pressure, without singularity. Also, it has been verified in more than thirty different solid-vapor adsorption systems.

On the other hand, during nonequilibrium processes, when a certain degree of undercooling is reached, gas-solid interfaces undergo adsorption phase transition, forming liquid films at the wetting interface. Most of the current research focuses on nucleation and control of saturated vapor condensation on solid surfaces under a certain degree of undercooling. Kashchiev et al. [38] pointed out that different adsorption properties can alter the wetting process of interfaces and provide wetting transition conditions at different temperatures, explaining the fundamental characteristics of adsorption from a thermodynamic perspective. Laaksonen [39], by combining the molecular adsorption cluster model, theoretically predicted the nucleation characteristics of water molecular adsorption clusters on solid surfaces under supersaturated conditions. The model's predicted results were in good agreement with classical heterogeneous nucleation theory. However, Laaksonen did not provide an explanation for the adsorption and cluster evolution process before nucleation occurs. Yu and Wang [40] studied the influence of nanoparticle surface curvature and wettability on water vapor condensation, exploring the two stages of condensation nucleation. The research findings revealed that the formation of water molecule clusters significantly enhances the nucleation rate, while particle surface curvature and wettability facilitate cluster growth, although cluster coalescence reduces the nucleation rate. Most of the aforementioned studies focused on water vapor nucleation and condensation on solid substrates, while the mechanisms and related theoretical models of adsorption phase transition have been rarely discussed.

The adsorption and cluster evolution processes before nucleation occurs are also crucial for the study of gas-solid interface adsorption. Understanding these processes is important for revealing the initial stages of adsorption, the formation of adsorbate clusters, and their subsequent evolution. The zeta model provides a new solution that can

address these issues and offer a more comprehensive theoretical framework. The molecular cluster zeta model serves as a theoretical basis for obtaining the distribution of adsorbate clusters on gas-solid interfaces, the wetting pressure ratio during interface adsorption phase transition, and the calculation of solid surface tension under zero adsorption conditions.

In summary, the zeta model offers a new perspective and theoretical framework to address the mechanisms and related issues of adsorption phase transition. By studying and applying this model, we can gain a better understanding of various phenomena in the adsorption phase transition process and provide a more accurate and comprehensive theoretical basis for the design and control of adsorption processes. Hence, we have undertaken a comprehensive examination of the zeta adsorption model, which is rooted in statistical mechanics principles applied to gas-solid interfaces, as well as the mechanism governing the phase transition in gas-solid adsorption.

2. Zeta Adsorption Model Based on Statistical Mechanics

Zeta adsorption model provides new insights into the adsorption models of gas-solid interfaces from the perspectives of quantum mechanics and statistical thermodynamics. The zeta adsorption model, proposed by Ghasemi and Ward [41], offered fresh insights into the adsorption models of gas-solid interfaces by incorporating principles from quantum mechanics and statistical thermodynamics. It presents a novel approach to adsorption where gas molecules adsorb in clusters onto specific adsorption sites, unlike the multilayer adsorption described by the BET model. This model considers the adsorption of molecular clusters at different adsorption sites (assuming that each cluster is a one-dimensional harmonic oscillator) and determines their partition function based on the most probable distribution of each cluster. This allows for the determination of the molecular distribution state of clusters with different numbers of molecules. The partition function establishes a connection between the quantum mechanical state of the molecular cluster and the macroscopic thermodynamic quantity and leads to the derivation of an adsorption isotherm based on the molecular cluster model. This model solves problems that other single-layer or multilayer adsorption models (empirical, semiempirical models) cannot address, such as infinite adsorption at the saturation vapor pressure and negative adsorption when the pressure exceeds the saturation vapor pressure. Additionally, the molecular cluster zeta adsorption model provides a theoretical basis for obtaining the distribution of adsorbed clusters at the gas-solid interface, the wetting pressure ratio when interface adsorption undergoes a phase transition, and the calculation of the surface tension of a solid under zero adsorption conditions.

To begin with, Ward and Wu [35] considered the various clusters of molecules adsorbed on a solid surface as one-dimensional harmonic oscillators with different frequencies. These clusters can be characterized by a set of

variables, a_k , representing the frequencies of the oscillations. The total energy, E , of the adsorbed molecules can be described in terms of these variables, a_k , and the number of phonons associated with each type of oscillator, I_k .

$$E(a_1, a_2, \dots, a_\xi, I_1, I_2, \dots, I_\xi) = \sum_{k=1}^{\xi} \left(3a_k \epsilon_0^{(k)} + I_k \hbar \omega^{(k)} \right). \quad (7)$$

Ward and Wu [35] approached the issue of thermal vibrations of atoms adsorbed on a solid surface by reformulating it as a problem involving quasiparticles known as phonons. In clusters where atoms are closely spaced, each atom experiences small oscillations around its equilibrium position. Consequently, Ward and Wu [35] introduced the concept of phonon modes to represent the vibrational modes of quantum harmonic oscillators within each cluster. These phonon modes capture the collective vibrational behavior of atoms within the clusters.

$$g_e = \frac{(3\alpha_k + I_k - 1)!}{(3\alpha_k - 1)!(I_k!)}. \quad (8)$$

In Ward's framework, the adsorption of gas molecules on a solid surface was viewed as the lattice vibrations of a crystal composed of k -clusters. These clusters were effectively represented as the vibrations of 3 a_k independent harmonic oscillators. Each vibrational mode of these oscillators was referred to as a normal mode of vibration. By employing the Bose-Einstein statistics, Ward calculated the number of microstates for the k nonlocalized phonons when k identical phonons were randomly distributed among the 3 a_k localized oscillators.

2.1. The Fundamental Assumptions and Derivation of Zeta Adsorption Model. At the solid-vapor interface, Ward and Wu [35] supposed there are M independent, distinguishable, and equivalent site adsorption sites per unit area, that as many as k -molecules may adsorb in a molecular cluster at one site and treat each cluster of k molecules as a chemical species, and each cluster is approximated as a three-dimensional, quantum mechanical, harmonic oscillator having a fundamental frequency that depends on the number of molecules in the cluster, $\omega^{(k)}$. Each cluster contains k molecules, and the maximum number of molecules in a single cluster is ζ . Each cluster can be viewed as a quantum harmonic oscillator, and its energy is related to the number of molecules contained in the cluster. They neglect the internal degrees of freedom of a cluster and approximate each cluster as a mass of $k \times m$, where m is the mass of a vapor molecule.

If a_k denotes the total number of type k clusters on the surface, $n^{SV}(x^V)$ is the amount adsorbed per unit area, and its value is independent of the specific area, A . It was then determined from

$$n^{SV} = \prod_{k=1}^{\zeta} k a_k. \quad (9)$$

The amount of vapor adsorbed per unit area of the substrate can be obtained by summing the product ka_k over all of the cluster types. If the number of empty adsorption sites is denoted as a_0 , then

$$a_0 = M - \sum_{k=1}^{\zeta} a_k, \quad (10)$$

where a_k is the number of clusters with k molecules.

According to the law of conservation of total energy, the energy levels of each degree of freedom of a cluster may be written as follows:

$$\begin{aligned} \epsilon_j^{(k)} &= \epsilon_0^{(k)} + j\hbar\omega^{(k)}, \\ j &= 0, 1, 2, 3, \dots; k = 1, 2, 3, \dots, \zeta. \end{aligned} \quad (11)$$

$\epsilon_0^{(k)}$ is the zero-point energy of each degree of freedom of a cluster of k molecules, and \hbar denotes the Planck constant divided by 2π .

They suppose the partition function for a type k cluster may be written as a product:

$$q_k = q_1(q_v)^{k-1}, \quad k = 2, 3, \dots, \zeta, \quad (12)$$

where the partition function for a single adsorbed molecule is q_1 . q_k is the partition function for a component with k molecules, and the cluster-size distribution.

From the relation between the Helmholtz function and the canonical partition function, the chemical potential expression of the adsorbed clusters containing k molecules may be found by differentiating the partition function [36] with respect to a_k .

$$\mu_i = \left(\frac{\partial A}{\partial N_i} \right)_{T,V,N_{i \neq \alpha}} = -kT \left(\frac{\partial \ln Q}{\partial N_i} \right)_{T,V,N_{i \neq \alpha}} = kT \ln \left(\frac{a_k}{a_0 q_k} \right). \quad (13)$$

Under equilibrium conditions between clusters consisting of k molecules and the clusters containing only one molecule

$$\mu_k = k\mu_1 = k\mu^V. \quad (14)$$

By using Eqs. (13) and (14), the ratio a_k/a_1 of may be expressed as a function of their chemical potential difference and the ratio of their respective partition functions.

$$\frac{a_k}{a_1} = \frac{q_k}{q_1} \exp \left[\frac{(\mu_k - \mu_1)}{k_b T} \right]. \quad (15)$$

From Eqs. (12), (13), and (14),

$$\frac{a_k}{a_1} = (\alpha x^V)^{k-1}, \quad (16)$$

$$\alpha \equiv q_v \exp \frac{\mu(T, P_s)}{k_b T}. \quad (17)$$

Note that α is a single function of temperature.

The expression for the number of empty adsorption sites a_0 as a function of x^V is given by

$$a_0 = M - \frac{a_1 \left[(\alpha x^V)^\zeta - 1 \right]}{(\alpha x^V - 1)}. \quad (18)$$

An expression for a_1 is obtained by Eq. (15) as

$$k_b T \ln \left(\frac{a_1}{a_0 q_1} \right) = k_b T \ln \left(\frac{\alpha x^V}{q_v} \right), \quad (19)$$

substitute Eq. (19) into Eq. (20) and solving for a_1

$$\frac{a_1}{M} = c \alpha x^V \left(1 - \left(\frac{a_1}{M} \right) \frac{(\alpha x^V)^\zeta - 1}{(\alpha x^V - 1)} \right), \quad (20)$$

where $c = q_1/q_v$.

Substitute Eq. (21) into Eq. (9) and solving for An^{SV}/a_1 .

$$\begin{aligned} \frac{An^{SV}}{a_1} &= \frac{\left[1 - (\alpha x^V)^\zeta \right] (1 - \alpha x^V)}{(1 - \alpha x^V)^2} \\ &+ \frac{\alpha x_i^V \left[1 - \zeta (\alpha x^V)^{\zeta-1} + (\zeta - 1) (\alpha x^V)^\zeta \right]}{(1 - \alpha x^V)^2}. \end{aligned} \quad (21)$$

Substitute Eq. (22) into Eq. (21), after simplifying,

$$n^{SV} = \frac{M c \alpha x^V \left[1 - (1 + \zeta) (\alpha x^V)^\zeta + \zeta (\alpha x^V)^{1+\zeta} \right]}{(1 - \alpha x^V) \left[1 + (c - 1) \alpha x^V - c (\alpha x^V)^{1+\zeta} \right]} \quad (22)$$

Ward and Wu [35] referred to the expression for n^{SV} , given in Eq. (22), as the zeta-isotherm relation. n^{SV} represents the amount adsorbed per unit area, and its value is independent of the specific area. Note that n^{SV} is given explicitly in terms of x^V , and the four isotherm constants: M , c , α , and ζ . M represents the number of interface adsorption units, which is solely dependent on the adsorbent material. ζ represents the number of molecules contained in a cluster. c and α are single-valued functions that depend only on temperature and are independent of the pressure variable. The NonlinearFit package in Mathematica is utilized to choose the parameter values. Due to the intricate nature of the isotherm equation, it was not possible to determine all four parameters simultaneously for each system under investigation. Therefore, we adopt a specific value for ζ and determine the values of M , c , and α that yield the closest agreement with the experimental measurements for that particular value of ζ .

2.2. *Application of the Zeta-Isotherm Model in Studying Adsorption Performance of Mesoporous Materials and Adsorption Properties on Nanomaterial Surfaces.* The zeta-isotherm model has been applied to investigate the adsorption behavior of gases and liquids in mesoporous materials. By considering the interactions between the adsorbate molecules and the pore walls, the zeta model provides insights into the adsorption capacity and in mesoporous materials.

Zandavi and Ward [42] based on zeta adsorption isotherms and applied it to investigate the adsorption process of two hydrocarbon vapors, octane and heptane, on two types of shale materials: untreated shale and ground shale. They determined the specific surface area and pore size distribution for both types of shale materials, approximating the pores as cylinders and calculating the average pore size.

Additionally, Zandavi and Ward [42] determined the adsorption isotherms of toluene on nonporous silica gel and mesoporous silica gel. Toluene and octane were exposed to nonporous silica gel and mesoporous silica gel samples, respectively, in the partial pressure range close to zero to 0.98. The adsorbed amount of toluene on nonporous silica gel was determined to be 2.5238 ± 0.0005 mg, and on mesoporous silica gel, it was 3.1241 ± 0.0005 mg. The adsorbed amount of octane on nonporous silica gel was 2.9162 ± 0.0005 mg, and on mesoporous silica gel, it was 3.0578 ± 0.0005 mg. The adsorption and desorption processes of both substances on the solids were studied.

For each vapor, it is noteworthy that the zeta adsorption isotherm accurately described the data across the entire x^V range. For comparison, the BET isotherm data in the high-pressure region were also shown alongside the zeta adsorption model. As expected, the BET isotherm only applied to the data for $x^V < 0.45$. In this case, the x^V max value described by the zeta adsorption model was 0.95, close to 1.

Ward and Wu [35] collected literature data on the adsorption of water vapor on silica (at 30°C), on alumina (at 20°C), and benzene on quartz (at 25°C) from different range of x^V . Then, using the collected data, Ward and Wu [35] performed linear fitting using Mathematica to obtain the four parameters required in Eq. (22). Subsequently, Ward used these parameters to generate the zeta adsorption isotherms and compared them with the original data. The theoretical adsorption curve and the experimental measurements exhibit good agreement within different pressure ratio ranges.

Narayanaswamy and Ward [43] conducted extensive linear fitting of the specific surface areas of different samples of given materials using the zeta isotherm model's four parameters. He investigated the adsorption of nitrogen gas on five different materials: silica, α -alumina, γ -alumina, carbon black, and graphitized carbon, resulting in a total of 19 different samples. For α -alumina, the zeta thermodynamic isotherm was determined using samples with specific surface areas ranging from 0.42 to 8.13 m²/g. Additionally, the adsorption properties of N₂ on nonoxide materials such as carbon black and graphitized carbon were also examined. The zeta isotherm's parameters for N₂ adsorption on three carbon black samples and five graphitized carbon samples were obtained through nonlinear regression analysis. These constants, along with the specific surface areas of each mate-

rial, were used to predict the corresponding zeta thermodynamic isotherms, which closely matched the experimental data points. The zeta thermodynamic isotherm of carbon black showed excellent agreement with 99 data points from three different samples, confirming the effectiveness of the zeta analysis. Similarly, the zeta thermodynamic isotherm of graphitized carbon described 105 data points from five different samples with specific surface areas ranging from 6 to 8 m²/g.

3. Adsorption Phase Transition Processes

3.1. *Equilibrium Molecular Cluster Distributions.* In the derivation of the zeta isothermal adsorption theory, it is known that the interface exists in the form of molecular clusters on the adsorbent surface. The distribution and evolution of zero adsorption units and adsorption clusters under different pressure ratios can be obtained [44].

From Eq. (18), the fraction of the sites that are empty may be written as

$$\frac{a_0}{M} = 1 - \sum_{k=1}^{\zeta} \left(\frac{a_k}{M} \right). \quad (23)$$

When Eq. (20) is combined, a_0/M may be expressed as

$$\frac{a_0}{M} = 1 - \frac{a_1}{M} \sum_{k=1}^{\zeta} (\alpha x^V)^{k-1}. \quad (24)$$

Solving Eq. (20), one obtains a_1 as a function of x^V and the four isotherm constants.

$$\frac{a_1}{M} = \frac{(\alpha x^V - 1)c\alpha x^V}{(\alpha x^V - 1) + c\alpha x^V((\alpha x^V)^{\zeta} - 1)}. \quad (25)$$

By combining Eq. (24) and Eq. (25), we can determine the fraction of empty adsorption sites predicted by Eq. (20).

$$\frac{a_0}{M} = \frac{(\alpha x^V - 1)}{\alpha x^V \left[1 + c \left((\alpha x^V)^{\zeta} - 1 \right) \right] - 1}. \quad (26)$$

From Eq. (26) and Eq. (16), we can derive the number of sites that are occupied by clusters containing k molecules.

$$\frac{a_k}{M} = \frac{c(\alpha x^V - 1)(\alpha x^V)^k}{\alpha x^V \left[1 + c \left((\alpha x^V)^{\zeta} - 1 \right) \right] - 1}. \quad (27)$$

Clusters with an equal number of molecules are considered to belong to the same "cluster type." When the pressure ratio x^V equals α^{-1} , distinct cluster types emerge, and the quantity of each cluster type can be determined using Eq. (27). According to Eq. (26) and Eq. (27), it can be observed that the number of zero adsorption units at the interface and the number of adsorption clusters are both dependent on the

pressure ratio. Therefore, it is possible to plot their distribution variations with respect to the pressure ratio [44].

Wei et al. [45] identified the distribution and evolution of zero-adsorption units and adsorption clusters at different pressure ratios. The study focused on investigating the distribution and evolution of zero-adsorption units and adsorption clusters under varying pressure ratios. It was found that when the pressure of the adsorbate phase is zero, there is no adsorption behavior at the interface, and all units are zero-adsorption units. As the pressure ratio increases, gas molecules start to adsorb onto the solid surface, leading to a continuous decrease in the number of zero-adsorption units, as shown in Figure 1. The reduction in the number of zero-adsorption units is more pronounced during the initial stage of adsorption, while the changes in the intermediate to high-pressure ratio range are relatively small. Additionally, the number of single-cluster units initially increases and then decreases. And when the pressure ratio is slightly greater than α^{-1} , the presence of small molecular clusters on the adsorption interface becomes nearly negligible. Comparing Figures 2 and 3, it was observed that in the low-pressure ratio region, the rapid decrease in the number of zero-adsorption units is attributed to the rapid filling of gas in the adsorption sites, resulting in a sudden increase in the number of single-cluster units. With further increase in the pressure ratio, the diversity of clusters increases, and the proportion of single-cluster units gradually decreases. At a pressure ratio of $x^V = 2.0$, the proportion of large molecular clusters reaches approximately 90%, and these clusters exhibit homogeneous properties resembling a liquid-like film. This indicates the occurrence of wetting transition at the gas-solid interface. When the pressure ratio exceeds α^{-1} by a small margin, the presence of small molecular clusters on the adsorption interface diminishes significantly. At a pressure ratio of $x^V = 2.0$, the majority of the clusters are composed of larger molecules, exhibiting uniform characteristics reminiscent of a liquid film. This observation suggests that a wetting transition occurs at the gas-solid interface.

The rate of change of the zeta isotherm with different values of α exhibits a maximum at α^{-1} , indicating the occurrence of phase transitions between phases. In summary, the parameter α in the zeta isotherm adsorption equation characterizes the ease of phase transitions between the different phases of the adsorbate. A value of α closer to 1 indicates a lower critical condition for phase transition at the interface, while a value further away from 1 indicates a higher critical condition for phase transition at the interface. As the pressure ratio approaches $1/\alpha$, different types of clusters begin to appear, and when x^V equals $1/\alpha$, the number of each cluster type becomes equal. With further increases in the pressure ratio, the clusters merge together, resulting in larger cluster sizes and a significant reduction in the number of cluster types [45]. This transition can potentially lead to the occurrence of wetting phenomena.

3.2. The Impact of the Strength of Solid-Fluid Interaction and Substrate Subcooling on Phase Transition from Adsorption to Condensation. The interfacial region plays a crucial role in studying phase transitions as it is closely related to the char-

acteristics of adsorption and the initiation of condensation. However, there is still a limited understanding of adsorbate structures or clusters at the molecular level. In the low-pressure range, gas adsorption on a solid surface maintains thermodynamic equilibrium, indicating a balanced state of the system. Nevertheless, as the pressure ratio approaches or exceeds $x^V > 1$, this equilibrium state becomes unsustainable. This critical zone represents the transition from adsorption to condensation, where gas molecules undergo a phase change.

To investigate this transition comprehensively, Wu et al. [46] employed a combination of the zeta adsorption model and molecular dynamics simulations. Wu et al.'s [46] focus was to understand the transition process from the equilibrium state to nonequilibrium states. Wu et al. particularly highlighted the importance of the temperature difference between the substrate temperature and the ambient temperature (ranging from 1 K to 20 K), as well as the strength of the solid-fluid interaction represented by β (ranging from 0.075 to 0.5), in the context of the adsorption to condensation transition. By conducting further investigations in the high-pressure range, Wu et al. [46] aimed to uncover the underlying mechanisms involved in the transition from adsorption to condensation, focusing on two primary aspects: the amount of adsorption and the structural properties of the adsorbate. Wu et al. observed the adsorption of argon (Ar) atoms on a solid zone consisting of four layers of gold (Au) atoms, which served as a background. The 12-6 Lennard-Jones (LJ) potential is applied for the interactions between Ar-Ar and Ar-Au atoms.

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (28)$$

where σ is the finite distance at which the interatomic potential equals zero, ϵ is the depth of the potential well, and r_{ij} is the intermolecular distance between atoms i and j . The interaction parameters between Ar and Au in the solid-fluid interface were estimated using the Lorentz-Berthelot criterion. The criteria provide values of $\sigma_{\text{Ar-Au}} = 3.002 \text{ \AA}$ for the distance parameter and $\epsilon_{\text{Ar-Au}} = \beta \sqrt{\epsilon_{\text{Ar}} \epsilon_{\text{Au}}}$ [47] for the energy parameter. The parameter β represents the bonding strength between the solid Au surface and the argon atom, and it plays a crucial role in adjusting the overall strength of the solid-fluid interaction. A higher value of β indicates a stronger surface wettability, reflecting the increased affinity and interaction between the solid surface and the adsorbed argon atoms. Wu et al. [46] believe that the subcooling ΔT , which is the temperature difference between the hot fluid at the top and the cold source, plays a significant role in the condensation of argon atoms on the solid surface. Wu et al. observe that in the equilibrium state of the adsorption system, argon particles near the solid surface are trapped, resulting in a higher particle density. However, as one moves further away from the solid surface, the impact of adsorption weakens, and the interactions among the free argon particles strengthen. As a result, in this

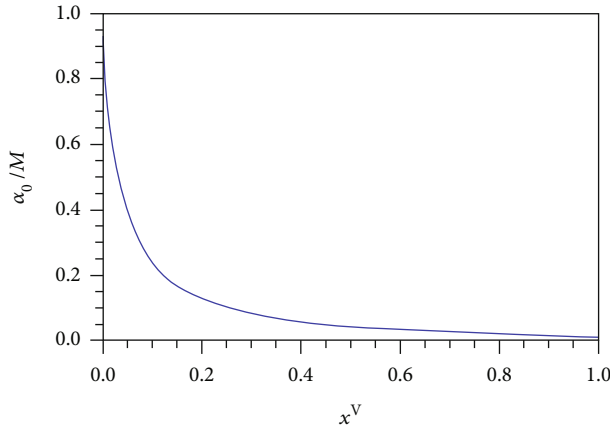


FIGURE 1: Empty sites vary with the pressure ratio.

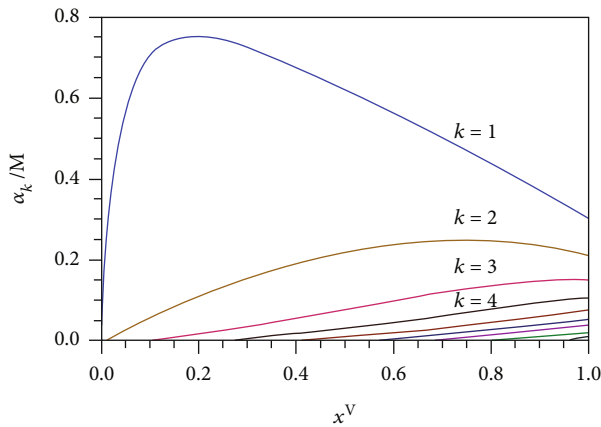
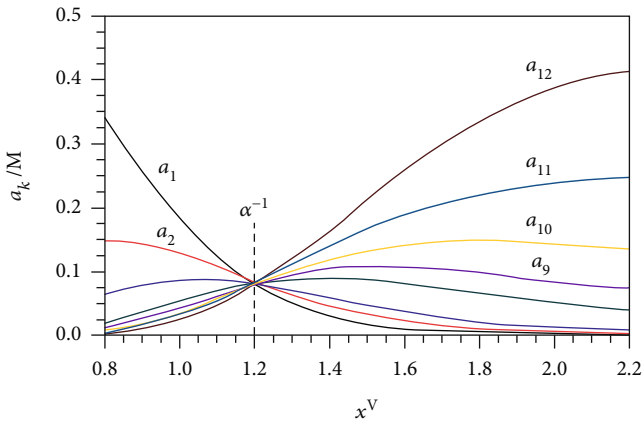


FIGURE 2: The variation of small molecular clusters with pressure ratio.

FIGURE 3: Cluster distribution when the pressure is around α^{-1} .

region, the free argon particles behave as a bulk fluid. It can be observed that for cases where ΔT is greater than 10 K, an additional stable density profile is observed in the region preceding the transition region, as indicated in Figure 4.

The density in this region closely approximates the saturation liquid density, indicating the occurrence of condensa-

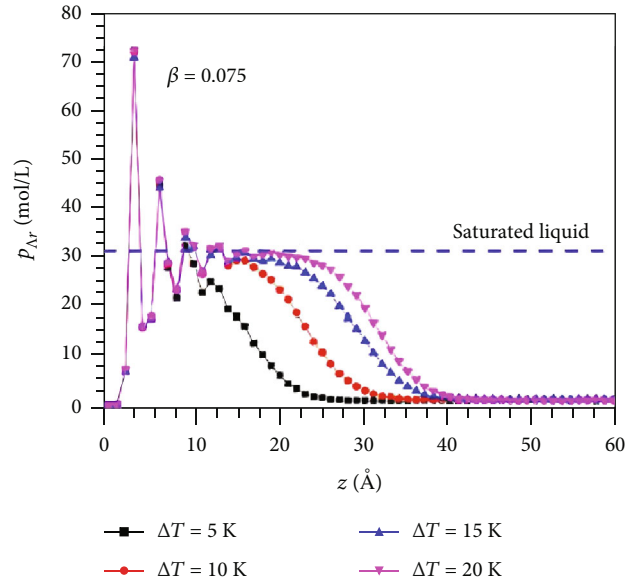


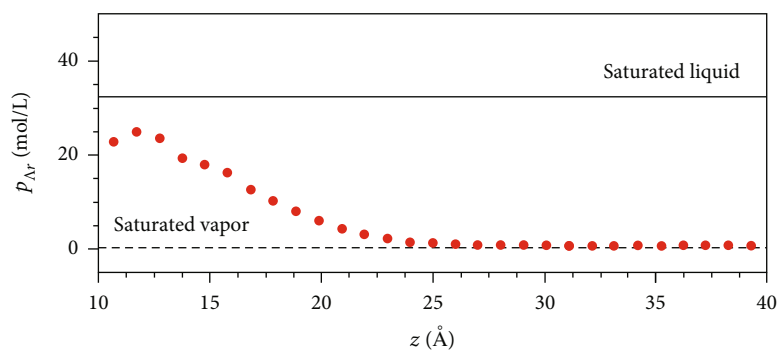
FIGURE 4: Density distributions with different combinations of temperature difference.

tion. Furthermore, in the case of $\beta = 0.075$, when ΔT exceeds 8 K, the density in a small region reaches the liquid line, indicating the initiation of condensate liquid formation. Therefore, 8 K is considered as the threshold temperature for condensation to occur. This aligns with the statement that ΔT greater than 10 K marks the onset of condensation.

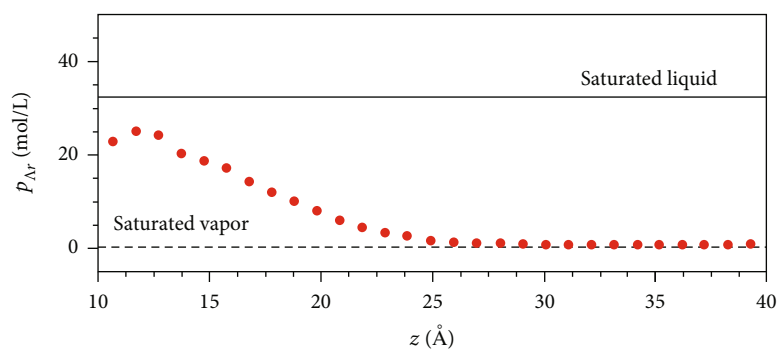
Figure 5 also precisely illustrates that 8 K is considered the threshold temperature for condensation to occur, because, as shown in Figures 5(d)–5(f) ($\beta = 0.075$), with temperatures above 8 K, the system undergoes condensation from the gas phase to the liquid phase.

Wu et al. pointed out that for small values of β , the weak adsorbed gas layer results in significant resistance for argon atoms to condense on the solid surface [46]. As a result, the adsorbed gas layer cannot transition into a condensed liquid phase until a sufficient subcooling is provided. This can be observed in Figure 6. As the value of β increases, indicating a stronger interfacial interaction, the adsorbed gas can undergo phase transition into a condensed liquid phase at lower subcooling levels. Additionally, with increasing subcooling, the adsorbed gas layer is more prone to condensation even under weaker interfacial interaction forces. Notably, when β exceeds 0.3, the strong solid-fluid interaction leads to a critical temperature difference for condensation of less than 1 K.

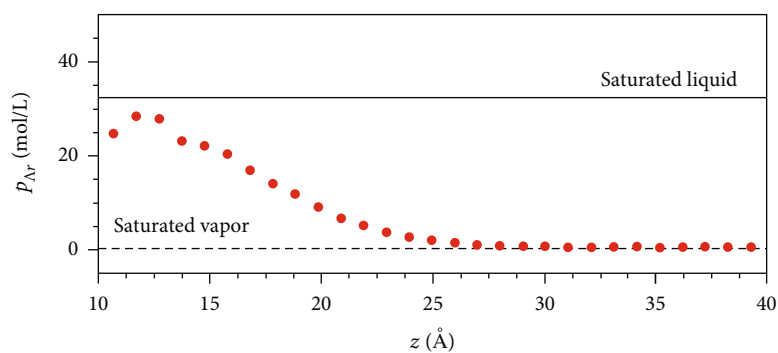
As depicted in Figure 7, the value of z_0 represents the distance from the solid surface. It gradually increases as the surface subcooling increases. However, as β increases, the curves become flatter, indicating a reduced growth rate of the condensation liquid layer. This is attributed to the stronger interfacial interaction between the gas and the solid surface. The interaction between argon molecules surpasses the interaction between argon and gold, leading to adsorption on the solid surface even with a small subcooling, resulting in the formation of molecular clusters and phase transition. The curves for β values of 0.3 and 0.5 exhibit



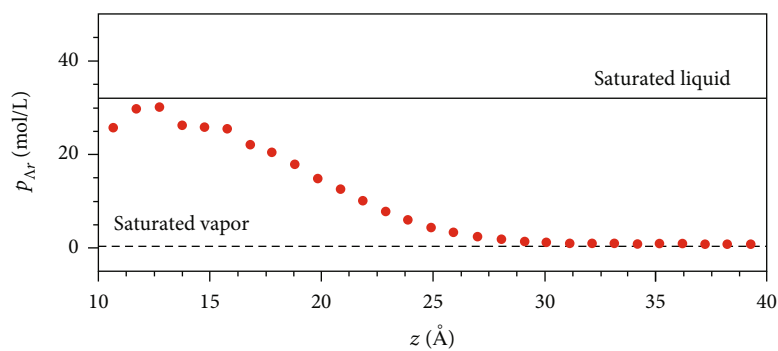
(a)



(b)



(c)



(d)

FIGURE 5: Continued.

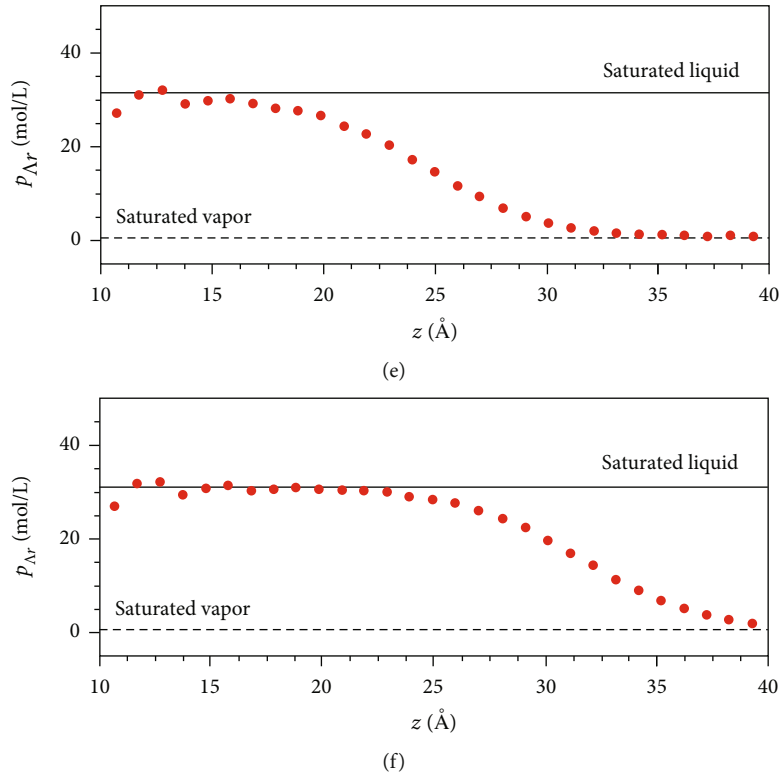


FIGURE 5: Initiation of liquid phase at different values of ΔT when $\beta = 0.075$. (a) 5 K, (b) 6 K, (c) 7 K, (d) 8 K, (e) 12 K, and (f) 20 K, respectively.

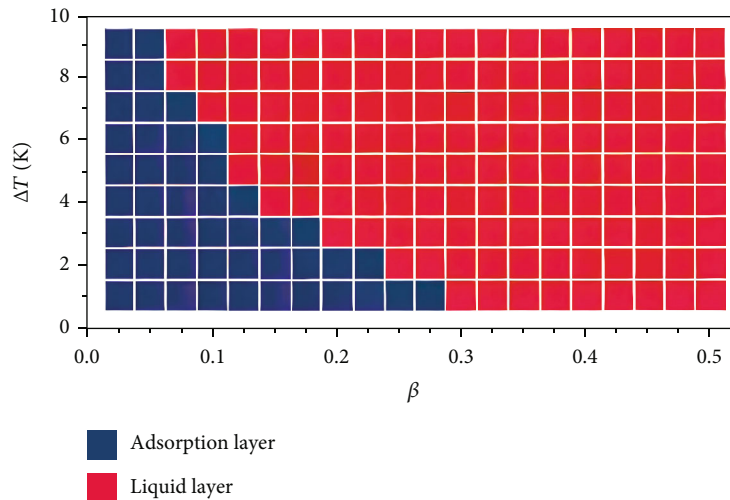


FIGURE 6: Variation of the positions of the Gibbs dividing surface for different values of temperature difference and β .

almost identical behavior, reflecting similar conditions. However, for lower β values such as 0.075, 0.1, and 0.15, the surface subcooling becomes crucial for condensation to occur and for the formation of the liquid layer. As the temperature difference increases, the condensation liquid layer thickens, and the transition region expands, leading to a more pronounced increase in the value of z_0 .

In conclusion, the temperature difference (surface subcooling) and the strength of solid-fluid interaction are two key factors that influence the transition process from

adsorption to condensation. Figure 7 summarizes the surface adsorption states with different combinations of β and ΔT .

3.3. Surface Tension at the Gas-Solid Interface γ^{SV} and the Solid Surface Energy γ^{SO} . According to the definition of wetting, at thermodynamic equilibrium, the three-phase contact line between gas, liquid, and solid should satisfy Young's equation. When the gas-solid interface undergoes a phase transition and transforms into a liquid-solid interface, the equilibrium contact angle θ_e at this point is referred to as

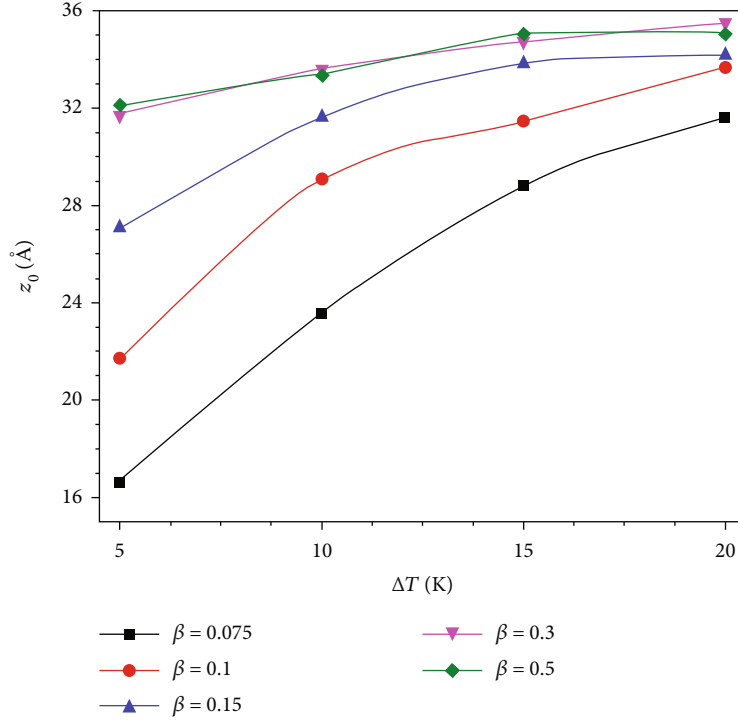


FIGURE 7: Variations of critical temperature difference with β for the transition from adsorption to condensation.

the wetting angle. The corresponding pressure ratio is accurately translated as the wetting pressure ratio, denoted as x^w .

$$\gamma^{sv} = \gamma^{sL} + \gamma^{Lv} \cos \theta_e. \quad (29)$$

The chemical potential of the vapor phase, μ^V , can be expressed as

$$\mu^V = \mu(P_s) + k_B T \ln x^V, \quad (30)$$

where P_s represents the chemical potential of the vapor phase at saturation pressure, and k_B is the Boltzmann constant. To assess the wetting conditions, the surface tension is evaluated by considering the impact of surface adsorption on the solid-vapor interface. This is accomplished by employing the Gibbs adsorption equation, which can be expressed as follows:

$$d\gamma^{sv} = -n^{sv} d\mu^{sv}. \quad (31)$$

For the gas-solid interface to undergo a phase transition and form a gas-liquid interface, it is necessary for the substrate temperature to be lower than the gas phase temperature inside the chamber. This is a necessary condition. Additionally, experimental conditions need to satisfy a pressure ratio greater than 1. However, in order to ensure approximate isothermal conditions during the gas-solid interface transition, the substrate temperature should be slightly lower than the gas phase temperature inside the chamber.

$$d\gamma^{sv}(x^v) = -n^{sv}(x^v) \frac{k_B T}{x^v} dx^v. \quad (32)$$

By combining the expression for n^{sv} given in Eq. (6), we obtain the following result:

$$\gamma^{sv}(x^v) = \gamma^{Lv} + M k_b T \ln \left(\frac{(1 - \alpha x^V)[1 + (c-1)\alpha x_w^V]}{(1 - \alpha x_w^V)[1 + (c-1)\alpha x^V]} \right). \quad (33)$$

The combination of the zeta isotherm equation and Gibbsian thermodynamics yields an expression for the surface tension of the solid-vapor interface, γ^{sv} , with x^V (the ratio of vapor-phase pressure to saturation vapor pressure) as the independent variable. Taking the limit of the γ^{sv} expression as x^V approaches zero gives the expression for γ^{s0} , the surface tension of the solid surface. The surface tension of a solid surface in the absence of adsorption, denoted as γ^{s0} , is an inherent characteristic of the solid material. Once the value of γ^{s0} is determined, the variation of γ^{sv} can be plotted, as shown in Figure 8. When the condensation liquid is formed, there exists a liquid-vapor interface where the surface tension, γ^{LV} , remains constant regardless of the bonding strength between the substrate surface and the adsorbed atom.

During Wei et al.'s [45] research on the variations of γ^{sv} for argon adsorbing on silicon with different surface orientations, it was discovered that adsorption reduces the surface tension of the solid-vapor interface from γ^{s0} to γ^{LV} , and determines the wetting conditions, as shown in Figure 8. As the adsorption amount at the interface gradually

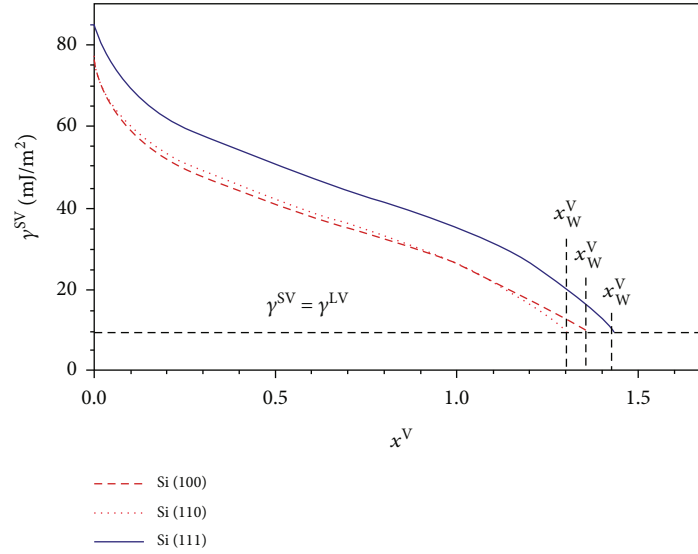


FIGURE 8: Variations of γ^{SV} for argon adsorbing on silicon with different surface orientations.

increases, the interfacial energy decreases, and the surface tension of the solid-gas interface decreases continuously until a solid-liquid interface is formed. On the other hand, near low-pressure ratios, the rapid increase in adsorption amount leads to a rapid decrease in the surface tension of the solid-gas interface. In the intermediate pressure ratio range, where the adsorption amount increases slowly, the surface tension of the solid-gas interface decreases slowly. Wetting conditions are determined by factors such as the strength of the solid-liquid interaction and the critical surface tension required for the liquid to cover the solid surface.

Narayanaswamy conducted research on the adsorption of N_2 vapor on the solid-vapor interfaces of silica and α -alumina substrates, as well as on carbon black and graphitized carbon at 77 K. The study also revealed a consistent decrease in the surface energy of the solid-vapor interface with increasing pressure ratio. Based on this point, we conclude that when the surface tension of the liquid-vapor interface is less than or equal to the surface tension of the solid-vapor interface, wetting occurs, allowing the liquid to completely cover and spread on the solid surface. This transition from nonwetting to wetting conditions is significant in surface science, as it influences the behavior and interactions of liquids on solid surfaces.

3.4. Assessing the Stability of Adsorbate through Molar Latent Heat. An interesting observation is made regarding the cooling effect on the adsorbate despite an increase in heating caused by adsorption. This phenomenon raises concerns about the stability of the adsorbate. To assess the thermodynamic stability of the adsorbate, researchers delve into the analysis of its latent heat, denoted as Λ_a^{SV} . This parameter provides a valuable measure for evaluating the thermodynamic characteristics and stability of the adsorbate under these conditions.

According to Narayanaswamy's previous work, it was found that the chemical potential per molecule of the adsorbate is greater than that of the vapor in the range of $1 \leq x^V$

$\leq \alpha^{-1}$, indicating that the adsorbate is in an unstable state. To further analyze the stability of the adsorbate, Narayanaswamy utilized Eq. (26) and Eq. (27) along with the ZAI constants to determine the entropy of the adsorbate as a function of x^V .

$$s^{SV}(x^V) = -k_B \sum_k^{\zeta} \left[\left(\frac{a_k(x^V)}{M} \right) \ln \left(\frac{a_k(x^V)}{M} \right) \right]. \quad (34)$$

Since $s^{SV}(0)$ is zero, the calculated heat of adsorbate, q_H^{SV} , can be expressed as

$$q_H^{SV}(0, x^V) = T s^{SV}(x^V). \quad (35)$$

The latent heat of the adsorbate, Λ_a , as a function of x^V , is determined based on the adsorbate heating. In other words, it is derived from the relationship between the heat generated during adsorption and the corresponding changes in the adsorbate.

$$\Lambda_a(x^V) = \frac{1}{N_0 k_B T} \left(\frac{\partial q_H^{SV}}{\partial x^V} \right)_T \quad (36)$$

Figure 9 illustrates the variation of the molar latent heat of Si-1000 silica, calculated using Eq. (36), as a function of x^V . In the range of x^V , where $1 \leq x^V \leq \alpha^{-1}$, the latent heat reaches its maximum and then sharply decreases until it becomes zero at x^V equal to α^{-1} . In the low-pressure range, the latent heat is negative, indicating the adsorbate is in an unstable state [48]. Similarly, when x^V equals α^{-1} , the latent heat becomes zero, and for x^V values greater than α^{-1} , the predicted latent heat remains negative. Beyond α^{-1} , Λ_a remains in the negative domain.

As mentioned in Section 3.1, when x^V reaches α^{-1} , the number of cluster types in the adsorbate becomes equal, and approximately every site is occupied, indicating the

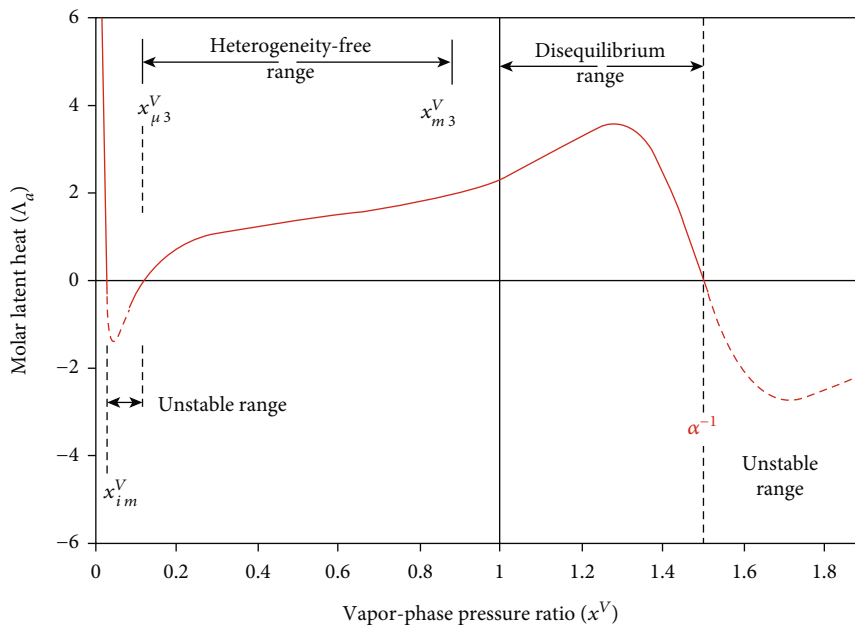


FIGURE 9: Latent heat as a function of x^V for Ar adsorbing on a silica sample.

initiation of the formation of threshold-sized clusters. This is considered to be the onset of the wetting transition, leading to the transformation of the adsorbed vapor into a liquid phase.

The instability of the adsorbate at this value of x^V and beyond is attributed to the formation of clusters with a critical size and the interactions among these adsorbed components. This triggers the transition of the adsorbate at the interface into a liquid phase that is adsorbed onto the surface. The analysis of molar latent heat further confirms the interpretation that the adsorbate is unstable when $x^V = \alpha^{-1}$.

4. Conclusion and Outlook

In this review, the significance of the zeta adsorption model in physics and its integration with statistical mechanics was investigated through the proposal and subsequent applications of the model to interface adsorption. Through analysis and simulations, the advantages of the zeta adsorption model in calculating solid surface tension, the evolution of cluster formation from small to large clusters with temperature and pressure, and the effects of interaction forces between the adsorbate and the surface, as well as surface subcooling, on the condensation process were comprehensively summarized. Furthermore, the unstable state during condensation was discussed based on the analysis of molar latent heat. The following conclusions can be drawn from the results.

- (1) The zeta adsorption model stands out from traditional models due to its ability to seamlessly extend into the thermal disequilibrium region without encountering singularities
- (2) The zeta-adsorption model, proposed by Ward, offered fresh insights into the adsorption models of

gas-solid interfaces by incorporating principles from quantum mechanics and statistical thermodynamics. Ward’s framework focuses on the adsorption of gas molecules on a solid surface as lattice vibrations of clusters, using the Bose-Einstein statistics to calculate the number of microstates for randomly distributed phonons among localized oscillators

- (3) The zeta adsorption model has also demonstrated remarkable applications in studying the adsorption performance of mesoporous materials and the adsorption properties on nanomaterial surfaces. As anticipated, the BET isotherm was only applicable to data points with $x^V < 0.45$. In contrast, the zeta adsorption model accurately described the data, with a maximum x^V value of 0.95, approaching 1
- (4) As the pressure ratio increases, the availability of empty adsorption sites decreases, leading to the formation of larger clusters in the adsorbate. At the pressure ratio of $1/\alpha$, each cluster type has an equal probability of occurrence, and nearly all adsorption sites become occupied. When the solid surface is completely occupied by homogeneous large clusters, a transition from adsorption to condensation takes place, triggering the wetting of the surface by the liquid phase
- (5) The molecular cluster zeta model provides a theoretical foundation for determining the distribution of adsorbate clusters on gas-solid interfaces, the wetting pressure ratio during the phase transition of interface adsorption, and the calculation of solid surface tension under conditions of zero adsorption. The determined n^{SV} are used with the Gibbs adsorption

equation to determine the solid surface energy, γ^{s0} , and solid–vapor interface energy, γ^{sv}

- (6) The parameter β represents the bonding strength between the solid surface and the adsorbed atoms. A higher β value indicates stronger surface wettability and increased interaction between the solid surface and the adsorbate. This parameter plays a crucial role in adjusting the overall strength of the solid–fluid interaction. Surface subcooling is also a crucial factor in studying interface phase transitions. Weak solid–gas interaction results in higher resistance for condensation on the solid surface, requiring sufficient surface subcooling for the transformation from adsorbed vapor to condensate liquid. Understanding the influence of these factors is important for designing and optimizing applications related to interface phase transitions
- (7) To assess the thermodynamic stability of the adsorbate, researchers delve into the analysis of its latent heat. The adsorbate becomes unstable beyond this value of x^V due to the formation of critical-sized clusters and the interactions among these adsorbed components

This leads to a transition of the adsorbate from the interface to a liquid phase, which is then adsorbed onto the surface. The analysis of molar latent heat provides additional evidence supporting the interpretation of adsorbate instability at $x^V = \alpha^{-1}$. Based on the findings of this study, there are several potential avenues for future research in the field of interface adsorption and the zeta adsorption model. Firstly, further investigations can be conducted to explore the applicability of the zeta model to different types of surfaces and adsorbates, including complex surfaces and multicomponent systems. This would provide a more comprehensive understanding of the adsorption behavior and its relation to the solid–gas interaction.

Additionally, the review can be extended to examine the dynamic processes of cluster formation and transition, taking into account the influence of factors such as temperature, pressure, and surface morphology. This would help elucidate the kinetics and mechanisms underlying the adsorption-to-condensation transition and provide insights into the temporal evolution of the adsorbed phases. Furthermore, the role of surface defects, heterogeneities, and impurities in the adsorption process can be investigated to better understand their impact on the stability and properties of the adsorbed layers. This could involve studying the effects of surface roughness, surface functionalization, and the presence of contaminants on the adsorption behavior. Moreover, the development of advanced computational methods and techniques can be explored to enhance the accuracy and efficiency of simulating interface adsorption using the zeta model. This could include the utilization of machine learning approaches or the incorporation of quantum mechanical calculations to capture finer details of the adsorption process.

Data Availability

The datasets analyzed in this study are publicly available. The “Application of the Zeta-isotherm Model in Studying Adsorption Performance of Mesoporous Materials and Adsorption Properties on Nanomaterial Surfaces” data supporting this systematic review is from previously reported studies and datasets, which have been cited. The processed data are available at Elsevier <https://doi.org/10.1016/j.jcis.2013.06.062> and ACS <https://doi.org/10.1021/acs.jpcc.1c08945>. “The Impact of the Strength of Solid–fluid Interaction and Substrate Subcooling on Phase Transition from Adsorption to Condensation” data supporting this systematic review is from previously reported studies and datasets, which have been cited. The processed data are available at Elsevier <https://doi.org/10.1016/j.ijheatmasstransfer.2021.121096>. The “Surface Tension at the Gas–Solid Interface γ^{SV} and the Solid Surface Energy γ^{S0} ” data supporting this systematic review is from previously reported studies and datasets, which have been cited. The processed data are available at Elsevier <https://doi.org/10.1039/C9CP07029J>.

Conflicts of Interest

The authors declare no competing conflicts of interest.

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References

- [1] J. Rouquerol, F. Rouquerol, and K. S. W. Sing, *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*, Academic press, 2013.
- [2] J. B. Hudson, *Surface science: an introduction*, John Wiley & Sons, 1998.
- [3] A. Mudhoo, A. Bhatnagar, M. Rantalankila, V. Srivastava, and M. Sillanp, “Endosulfan removal through bioremediation, photocatalytic degradation, adsorption and membrane separation processes: a review,” *Chemical Engineering Journal*, vol. 360, pp. 912–928, 2019.
- [4] D. Farrusseng, *Metal-organic frameworks: applications from catalysis to gas storage*, John Wiley & Sons, 2011.
- [5] K. A. Cychosz and M. Thommes, “Progress in the physisorption characterization of nanoporous gas storage materials,” *Engineering*, vol. 4, no. 4, pp. 559–566, 2018.
- [6] E. A. Vogler, “Practical use of concentration-dependent contact angles as a measure of solid–liquid adsorption. 1. Theoretical aspects,” *Langmuir*, vol. 8, no. 8, pp. 2005–2012, 1992.
- [7] P. A. Redhead, “An empirical isotherm for multilayer physisorption,” *Langmuir*, vol. 12, no. 3, pp. 763–767, 1996.
- [8] M. Thommes, R. Guillet-Nicolas, and K. A. Cychosz, “Physical adsorption characterization of mesoporous zeolites,” *Mesoporous Zeolites: Preparation, Characterization and Applications*, pp. 349–384, 2015.

- [9] I. Langmuir, "The constitution and fundamental properties of solids and liquids. Part I. Solids," *Journal of the American Chemical Society*, vol. 38, no. 11, pp. 2221–2295, 1916.
- [10] H. Freundlich and H. S. Hatfield, *Colloid and Capillary Chemistry*, Methuen and Co, Ltd., London, 1926.
- [11] R. Sips, "On the structure of a catalyst surface," *The Journal of Chemical Physics*, vol. 16, no. 5, pp. 490–495, 1948.
- [12] J. Toth, "State equation of the solid-gas interface layers," *Models in Chemistry*, vol. 69, pp. 311–328, 1971.
- [13] S. Brunauer, P. H. Emmett, and E. Teller, "Adsorption of gases in multimolecular layers," *Journal of the American Chemical Society*, vol. 60, no. 2, pp. 309–319, 1938.
- [14] W. Norde, "Adsorption of proteins from solution at the solid-liquid interface," *Advances in Colloid and Interface Science*, vol. 25, pp. 267–340, 1986.
- [15] P. M. V. Raja and A. R. Barron, *BET Surface Area Analysis of Nanoparticles*, Rice University, 2021.
- [16] R. Apak, S. Gorinstein, V. Böhm, K. M. Schaich, M. Özyürek, and K. Güçlü, "Methods of measurement and evaluation of natural antioxidant capacity/activity (IUPAC technical report)," *Pure and Applied Chemistry*, vol. 85, no. 5, pp. 957–998, 2013.
- [17] R. Bardestani, G. S. Patience, and S. Kaliaguine, "Experimental methods in chemical engineering: specific surface area and pore size distribution measurements—BET, BJH, and DFT," *The Canadian Journal of Chemical Engineering*, vol. 97, no. 11, pp. 2781–2791, 2019.
- [18] D. Dutta, S. Chatterjee, K. T. Pillai, P. K. Pujari, and B. N. Ganguly, "Pore structure of silica gel: a comparative study through BET and PALS," *Chemical Physics*, vol. 312, no. 1–3, pp. 319–324, 2005.
- [19] R. L. Tseng and S. K. Tseng, "Pore structure and adsorption performance of the KOH-activated carbons prepared from corncob," *Journal of Colloid and Interface Science*, vol. 287, no. 2, pp. 428–437, 2005.
- [20] K. S. W. Sing, "Adsorption methods for the characterization of porous materials," *Advances in Colloid and Interface Science*, vol. 76–77, pp. 3–11, 1998.
- [21] M. M. Dubinin and L. V. Radushkevich, "Fundamentals of the theory of adsorption in micropores of carbon adsorbents: Characteristics of their adsorption properties and microporous structures," *Carbon*, vol. 27, no. 3, pp. 457–467, 1989.
- [22] K. Mosher, J. He, Y. Liu, E. Rupp, and J. Wilcox, "Molecular simulation of methane adsorption in micro- and mesoporous carbons with applications to coal and gas shale systems," *International Journal of Coal Geology*, vol. 109–110, pp. 36–44, 2013.
- [23] P. S. Kumar, L. Korving, K. J. Keesman et al., "Effect of pore size distribution and particle size of porous metal oxides on phosphate adsorption capacity and kinetics," *Chemical Engineering Journal*, vol. 358, pp. 160–169, 2019.
- [24] X. Li, L. Zhang, Z. Yang, P. Wang, Y. Yan, and J. Ran, "Adsorption materials for volatile organic compounds (VOCs) and the key factors for VOCs adsorption process: a review," *Separation and Purification Technology*, vol. 235, article 116213, 2020.
- [25] S. Yaghoubian, C. A. Ward, and C. A. Ward, "Initiation of wetting, filmwise condensation and condensate drainage from a surface in a gravity field," *Physical Chemistry Chemical Physics*, vol. 19, no. 31, pp. 20808–20817, 2017.
- [26] N. Vasiraja, R. S. S. Prabhakar, and A. Joshua, "Preparation and physio-chemical characterisation of activated carbon derived from *Prosopis juliflora* stem for the removal of methylene blue dye and heavy metal containing textile industry effluent," *Journal of Cleaner Production*, vol. 397, article 136579, 2023.
- [27] K. S. Obayomi, S. Y. Lau, O. Ibrahim et al., "Removal of Congo red dye from aqueous environment by zinc terephthalate metal organic framework decorated on silver nanoparticles-loaded biochar: mechanistic insights of adsorption," *Microporous and Mesoporous Materials*, vol. 355, article 112568, 2023.
- [28] T. Islamoglu, K. B. Idrees, F. A. Son et al., "Are you using the right probe molecules for assessing the textural properties of metal-organic frameworks," *Journal of Materials Chemistry A*, vol. 10, no. 1, pp. 157–173, 2021.
- [29] S. S. Dukhin, G. Kretzschmar, and R. Miller, *Dynamics of adsorption at liquid interfaces: theory, experiment, application*, Elsevier, 1995.
- [30] A. Clark, *The Theory of Adsorption and Catalysis*, Academic, 2018.
- [31] R. B. Perry, "Principles of colloid and surface chemistry, second edition (Hiemenz, P. C.)," *Journal of Chemical Education*, vol. 64, no. 12, p. A328, 1987.
- [32] A. B. D. Cassie, "Multimolecular absorption," *Transactions of the Faraday Society*, vol. 41, pp. 450–458, 1945.
- [33] R. B. Anderson, "Modifications of the Brunauer, Emmett and Teller equation1," *Journal of the American Chemical Society*, vol. 68, no. 4, pp. 686–691, 1946.
- [34] X. Wei, C. M. Wu, and Y. R. Li, "Characterizing on the interfacial thermal transport through adsorption clusters and vibrational behaviors," *International Journal of Heat and Mass Transfer*, vol. 183, p. 122086, 2022.
- [35] C. A. Ward and J. Wu, "Effect of adsorption on the surface tensions of solid-fluid interfaces," *The Journal of Physical Chemistry B*, vol. 111, no. 14, pp. 3685–3694, 2007.
- [36] T. L. Hill, *An introduction to statistical thermodynamics*, Courier Corporation, 1986.
- [37] K. S. W. Sing, "Assessment of surface area by gas adsorption," *Adsorption by Powders and Porous Solids*, vol. 2, pp. 237–268, 2014.
- [38] D. Kashchiev, P. G. Vekilov, and A. B. Kolomeisky, "Kinetics of two-step nucleation of crystals," *The Journal of Chemical Physics*, vol. 122, no. 24, p. 244706, 2005.
- [39] A. Laaksonen, "A unifying model for adsorption and nucleation of vapors on solid surfaces," *The Journal of Physical Chemistry A*, vol. 119, no. 16, pp. 3736–3745, 2015.
- [40] J. Yu and H. Wang, "A molecular dynamics investigation on evaporation of thin liquid films," *International Journal of Heat and Mass Transfer*, vol. 55, no. 4, pp. 1218–1225, 2012.
- [41] H. Ghasemi and C. A. Ward, "Surface tension of solids in the absence of adsorption," *The Journal of Physical Chemistry B*, vol. 113, no. 38, pp. 12632–12634, 2009.
- [42] S. H. Zandavi and C. A. Ward, "Contact angles and surface properties of nanoporous materials," *Journal of Colloid and Interface Science*, vol. 407, pp. 255–264, 2013.
- [43] N. Narayanaswamy and C. A. Ward, "Specific surface area of Nanopowders from argon adsorption at 77 and 87 K: zeta adsorption isotherm approach," *The Journal of Physical Chemistry C*, vol. 125, no. 51, pp. 28115–28135, 2021.
- [44] C. Wu, S. H. Zandavi, and C. A. Ward, "Prediction of the wetting condition from the zeta adsorption isotherm," *Physical Chemistry Chemical Physics*, vol. 16, no. 46, pp. 25564–25572, 2014.

- [45] X. Wei, C. M. Wu, and Y. R. Li, "Molecular insight into the formation of adsorption clusters based on the zeta isotherm," *Physical Chemistry Chemical Physics*, vol. 22, no. 18, pp. 10123–10131, 2020.
- [46] C. M. Wu, X. Wei, and Y. R. Li, "Investigation on the mechanisms of cluster formation and transition from adsorption to condensation," *International Journal of Heat and Mass Transfer*, vol. 171, p. 121096, 2021.
- [47] J. A. Templeton, R. E. Jones, J. W. Lee, J. A. Zimmerman, and B. M. Wong, "A long-range electric field solver for molecular dynamics based on atomistic-to-continuum modeling," *Journal of Chemical Theory and Computation*, vol. 7, no. 6, pp. 1736–1749, 2011.
- [48] N. Narayanaswamy and C. A. Ward, "Thermodynamic N₂vapor isotherms of materials: zeta adsorption isotherm approach," *The Journal of Physical Chemistry C*, vol. 125, no. 15, pp. 8440–8455, 2021.