

Adsorption Behavior of Repulsive Molecules

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Recently, it has been shown that adsorption of gases on solid surfaces often leads to repulsive forces between adsorbate molecules. In this paper, adsorption of molecules on a one-dimensional lattice is considered for repulsive interactions between adsorbate molecules. Exact adsorption isotherms are calculated and analyzed for finite and infinite chains of active sites (i.e., a one-dimensional lattice). Although the mathematical solution for the one-dimensional lattice is known for attractive and repulsive systems, the effects of intermolecular repulsions on adsorption behavior have not been studied in detail previously. Similarly, though the mathematics for the one-dimensional lattice has been solved for any arbitrary lattice length, the effect of finite size on adsorption isotherms for repulsive adsorbate interactions has never been examined. This paper shows that spatial confinement and strong attraction to active sites can cause compression of an adsorbed phase and that repulsive interactions between adsorbed molecules result in steps in the adsorption isotherms. For higher chemical potentials, the density increases until saturating at the lattice capacity. These steps in the adsorption isotherm have not been observed in previous studies of lattice systems. For small lattices, the adsorption behavior was found to be fundamentally different for even and odd values of lattice length. Lattices with an even number of lattice sites can have two steps in the adsorption isotherm, whereas systems with an odd number of sites only have a single step occurring at a coverage slightly greater than half the lattice capacity.

Introduction

Lattice models have been used extensively to analyze physical adsorption of fluids on solid surfaces.^{1–3} Classical elements of adsorption behavior predicted by lattice models include (but are not limited to)^{4–8}

- (a) Henry's law limit at small concentrations,⁷
- (b) Langmuir-like behavior for no interactions between nearest neighbors within the adsorbed monolayer,⁹
- (c) two-dimensional condensation (wetting phase transitions) for attractive interactions in adsorbed monolayers,^{10,11}
- (d) multilayer adsorption, capillary condensation, and hysteresis.^{12–16}

Historically, many theories of adsorption have been extensions of the Langmuir model made by including the effects of attractive interactions between adsorbate molecules.^{5–8} Attractive interactions are crucial for modeling multilayer adsorption and phase changes in the adsorbed layer. However, nearest neighbor repulsions also are possible under many conditions for adsorbate molecules on crystalline surfaces.^{17,18} These repulsions can result in ordered phases and order–disorder transitions.

Intermolecular repulsions are important in the phenomena of adsorption compression.^{19,20} In compressed systems, molecules adsorb to a highly attractive surface to reach densities greater than those in a normal liquid. Strong attractions to the surface can cause more molecules to pack in the fast layer than in a normal liquid and therefore create highly repulsive interactions among nearest neighbors. Adsorption to the surface continues until the decrease in free energy from molecule surface interactions is balanced by the increase free energy due to repulsions when bringing another molecule to the monolayer.

Adsorption compression has been confirmed experimentally by direct measurements of the differences between the lattice spacing on a substrate and in the bulk phase. Direct measurement of compression have been made for gas/solid adsorption,^{21–23} underpotential depositions in metal/metal systems,^{24,25} and for chemically adsorbed systems.^{26,27}

In addition to reduced lattice parameters of the adsorbed phase and strong molecular repulsions, adsorption compression has indirect experimental manifestations. It has been found that BET measurements for the adsorption of pentane, argon, krypton, and nitrogen on various adsorbents show that the area per molecule in the full monolayer decreases as the molecule–surface interaction energy increases,^{28,29} implying monolayer capacity can be a function of energetics. Studies also have shown that the differential heat of adsorption vanishes as the monolayer reaches maximum capacity,³⁰ due in part to increasing adsorbate–adsorbate repulsions as coverage increases. Additionally, analysis of experimental isotherms for many systems (such as nitrogen, carbon dioxide, methane, butane, ethylene, acetylene, benzene on silica gel, activated carbon, zeolites) indicate repulsive interactions within the adsorbed phase.¹⁶

This paper studies the compression of an adsorbed phase for a one-dimensional Ising system. Although the one-dimensional system with nearest neighbor interactions allows an exact solution for attractive and repulsive interactions, the effects of repulsive interactions have not been given significant attention. In this paper, we set the nearest neighbor interactions strengths (which are a function of intermolecular spacing) to be repulsive and then examine the effect of these repulsions on the adsorption isotherm. The effect of lattice length on the behavior of the adsorbed phases also is studied. This is important for the study of adsorption on materials with nanometer length scales. These

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effects of repulsive interactions and finite size on the adsorption properties of lattice systems have not been studied in detail previously.

One-Dimensional Lattice

The one-dimensional lattice model with nearest neighbor interactions is known to allow an exact solution for both attractive and repulsive interactions.^{31,32} For this reason, it not only has historical significance but also can be used for rigorous analysis of one-dimensional molecular systems or systems where elements of a larger model are represented by one-dimensional arrays. For example, this approach was used for the modeling of multilayer adsorption by Hill,¹⁴ and by Yagov and Lopatkin³³ where the authors considered a one-dimensional lattice gas, imposed a boundary condition at one end (at the surface), and calculated the Gibbs adsorption. Their results gave rigorous calculations for excess thermodynamic functions and provided new insights into the behavior of the Gibbs integral near saturation.

The approach used in this paper is different from the multilayer study of Hill because for our system all adsorbed molecules are in contact with the surface. The derivation of the grand partition function used in this paper is similar to the method used by other research groups, including Hock and McQuistan³⁴ and Phares and Wunderlich.³⁵ These authors have calculated the grand partition function exactly for a variety of quasi two-dimensional systems that have finite width in one direction and the second direction extending to infinity. They have studied the effects of nearest-neighbor, second-neighbor,³⁶ third-neighbor,³⁷ as well as the effect of different types of boundary conditions.^{17,38} Systems with both attractive and repulsive interactions have been studied,³⁴ but the effect that repulsive interactions have on the adsorption isotherm has not been examined in detail previously. Also, accounting for finite size on thermodynamic properties of the system has been demonstrated,³⁹ but these effects have never been analyzed for adsorption isotherms.

For this paper, we extend the theory of one-dimensional lattices to study the effects that repulsive interactions and lattice length have on the adsorption isotherm. We are interested specifically in the role of repulsions and compression on the behavior of the adsorbed phase. Compression for a lattice system implies that the substrate is imposing an intermolecular separation distance in the adsorbed-phase lattice that is significantly less than the minimum of the intermolecular potential of the adsorbing molecules. Thus compression is introduced by having repulsive nearest neighbor interactions. This paper is the first to use lattice models to study the effect that intermolecular repulsions have on the compression of an adsorbed phase and also is the first to show the importance of system length on the adsorption isotherm.

Grand Canonical Partition Function

The derivation for the grand partition function is similar to the method used by Hock and McQuistan³⁴ for the study of quasi two-dimensional lattices. Consider a one-dimensional lattice with N lattice sites and j molecules occupying those sites. We denote the canonical partition function of this system as $Q_{j,N}$. Adsorbed molecules have chemical potential μ , with nearest neighbor interactions of energy ϵ , and surface interactions with energy ϵ_s . The reduced chemical potential for an adsorbed molecule is defined as

$$\mu' \equiv \mu - \epsilon_s \quad (1)$$

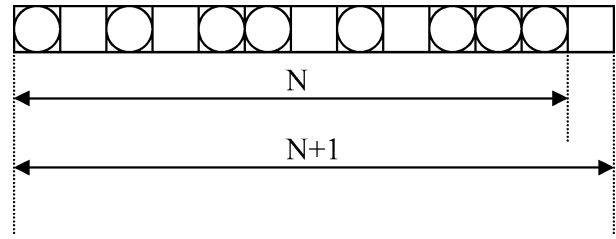


Figure 1. Changing the length from N to $N + 1$ and the keeping number of molecules, n , constant.

The thermodynamic activities are defined as

$$z \equiv e^{\mu'/kT} \quad \text{and} \quad x \equiv e^{-\epsilon/kT} \quad (2)$$

Similar to the method of Hock and McQuistan,³⁴ $Q_{j,N+1}$ is calculated from $Q_{j,N}$ by considering the additional configurations created by increasing the length of the lattice by one site as illustrated in Figure 1.

The $(N + 1)$ th lattice site either can be occupied or empty. If the site is empty, then the canonical partition function for this set of configurations is equal to $Q_{j,N}$. If the $(N + 1)$ th site is occupied by one of j molecules sitting on the lattice, then the canonical partition function for the lattice with N sites is $Q_{j-1,N}^*$ (* represents the presence of a molecule of site $N + 1$). Q and Q^* are related through the recurrence:

$$Q_{j,N+1} = Q_{j,N} + Q_{j-1,N}^* \quad (3)$$

This is because the set of configurations $(j, N + 1)$ consists of the sets (j, N) and $(j - 1, N)^*$.

When the $(N + 1)$ th site is occupied by a molecule, the N th site can be occupied or empty; so, the set $(j - 1, N)^*$ consists of sets $(j - 1, N - 1)$ and $(j - 2, N - 1)^*$ giving the recurrence relationship

$$Q_{j-1,N}^* = Q_{j-1,N-1} + xQ_{j-2,N-1}^* \quad (4)$$

The factor of x represents interaction between nearest neighbor molecules. Combining eqs 2 and 3 by eliminating Q^* results in the recurrence:

$$Q_{j+1,N+1} - Q_{j+1,N} - xQ_{j,N} + (x - 1)Q_{j,N-1} = 0 \quad (5)$$

Equation 5 is a partial difference equation whose general solution depends on both the number of adsorbed molecules and on the size of the lattice. To transform eq 5 to an ordinary difference equation, all terms are multiplied by z^j and summed from $j = 0$ to $j = N - 1$ giving

$$(\Xi_N - Q_{0,N} - z^N Q_{N,N})z - (\Xi_{N-1} - Q_{0,N-1})z - (\Xi_{N-1} - z^{N-1} Q_{N-1,N-1})x + (\Xi_{N-2} - Q_{0,N-2})(x - 1) = 0 \quad (6)$$

where Ξ_N is the grand partition for a lattice with N sites and is related to the canonical partition function by

$$\Xi_N = \sum_{j=0}^N z^j Q_{j,N} \quad (7)$$

Taking into account that

$$Q_{0,N} = 1 \text{ and } Q_{N,N} = x^{N-1} \quad (8)$$

Equation 6 gives

$$\Xi_N - (1 + xz)\Xi_{N-1} + z(x-1)\Xi_{N-2} = 0 \quad (9)$$

Equation 9 is a second-order ordinary difference equation with the general solution

$$\Xi_N = A_1\omega_1^N + A_2\omega_2^N \quad (10)$$

where A_1 and A_2 are arbitrary constants and ω_1 and ω_2 are the solutions to the equation

$$\omega^2 - (1 + xz)\omega + z(x-1) = 0 \quad (11)$$

which has known roots⁴⁰

$$\omega_1 = \frac{1 + xz + \sqrt{4z + (1 - xz)^2}}{2}$$

$$\omega_2 = \frac{1 + xz - \sqrt{4z + (1 - xz)^2}}{2} \quad (12)$$

The constants A_1 and A_2 are calculated by applying the boundary conditions

$$\Xi_0 = 1, \Xi_1 = 1 + z \quad (13)$$

which gives

$$A_1 = \frac{1 + 2z - xz + \sqrt{4z + (1 - xz)^2}}{2\sqrt{4z + (1 - xz)^2}}$$

$$A_2 = \frac{-1 - 2z + xz + \sqrt{4z + (1 - xz)^2}}{2\sqrt{4z + (1 - xz)^2}} \quad (14)$$

Adsorption Isotherms

The average density of adsorbed molecules is defined as

$$\rho = \frac{1}{N} \frac{\partial \ln \Xi_N}{\partial \ln z} \quad (15)$$

In the thermodynamic limit, the grand partition function is dominated by the largest root giving the classical result⁴⁰

$$\rho_{N \rightarrow \infty} = \frac{\partial \ln \omega_1}{\partial \ln z} = \frac{2z - (1 - xz)xz + xz\sqrt{4z + (1 - xz)^2}}{4z + (1 - xz)^2 + (1 + xz)\sqrt{4z + (1 - xz)^2}} \quad (16)$$

Figure 2 shows adsorbed density ρ for an infinitely long one-dimensional lattice as a function of the reduced chemical potential for various strengths of adsorbate–adsorbate interactions (note that the value for the adsorbate–surface interaction does not effect the shape of the adsorption isotherm). As seen in Figure 2, strong repulsions result in dramatic deviations from Langmuir-like behavior ($x = 1$) with the adsorption isotherm having a step at half capacity, and then reaching maximum capacity for greater values of the chemical potential. Repulsive interactions imply that the spacing between adsorbate molecules on nearest neighbor lattice sites is less than the intermolecular spacing in a normal liquid. Thus when the adsorbate density reaches the lattice capacity, the adsorbed molecules are com-

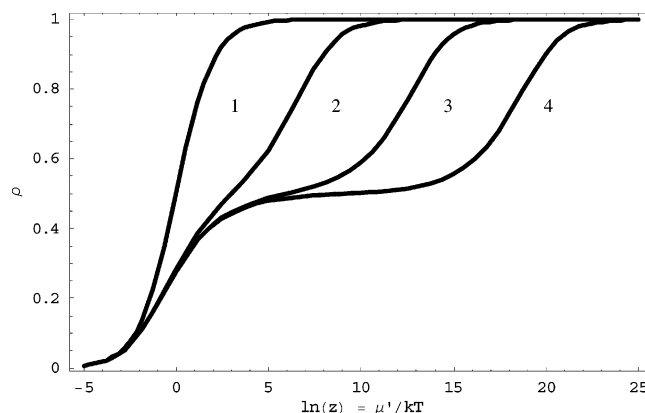


Figure 2. Adsorbed density as a function of reduced chemical potential for an infinite one-dimensional lattice with repulsive interaction energies of $\epsilon/kT = 0(1), 3(2), 6(3), 9(4)$.

pressed relative to a normal liquid, thus showing that adsorption compression can occur in lattice systems.

These isotherms are valid for systems at pressures in the undersaturated region, where the adsorbate–surface attraction is sufficient to have full monolayer adsorption before multilayer formation. These isotherms are also valid for systems where second and higher layers cannot form due to spatial limitations, for example, in slit like nanopores of activated carbon.⁴¹

Analogy to Adsorption on Active Sites

The results shown in Figure 2 for the compression of repulsive molecules on a lattice are similar to previous results for the adsorption compression of soft (Lennard-Jones) molecules.¹⁹ To illustrate this similarity, consider two active sites on the surface that can be occupied by molecules. If the distance between the active sites is large, adsorbate molecules can occupy both sites independently. If the sites are too close, then a molecule will occupy one site but block adsorption on the other site. When the active sites are close and their attraction of adsorbate molecules is strong, both sites can be occupied with repulsions between adsorbed molecules. In this case, attraction to the active sites must be strong enough to compensate for the repulsion between neighbors. Therefore, adsorption of both molecules simultaneously is thermodynamically favorable; however, the distance between such molecules is smaller than that in a normal liquid and adsorbate molecules repel each other. This is the simplest case of adsorption compression, and it can occur whenever the lattice spacing for molecules in the adsorbent is less than the minimum in the potential function for adsorbate–adsorbate interactions.^{19,20}

As mentioned previously, historically, adsorption models developed as extensions of the Langmuir model derived by including nearest neighbor interactions.^{5–8} For attractive interactions, in the framework of the monolayer model, this allowed predictions of the phenomenon of two-dimensional condensation (wetting phase transitions).¹¹ However, similar analysis for repulsive interactions has never been published, and the shape of the adsorption isotherm has not been studied in detail. The present paper performs this task and the outcome is that repulsions result in the phenomenon of adsorption compression.

Note that the Langmuir lattice model can be considered zero-dimensional because monolayer molecules do not interact—the occupation of each lattice site is independent of the occupation of neighboring sites. Imposing interactions can change the dimensionality of the system. In particular, the two active site model is still zero-dimensional, and the model in Figure 1 is

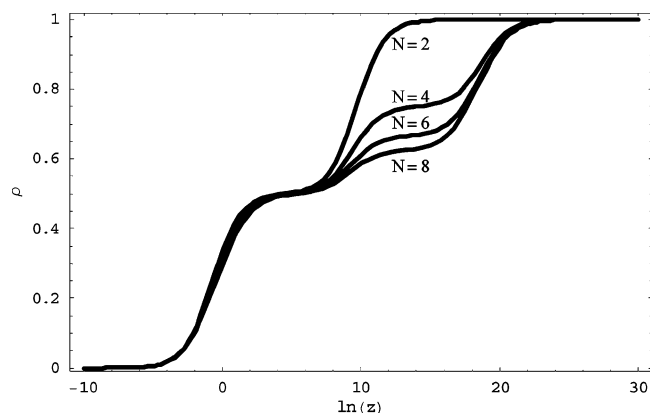


Figure 3. Adsorbed density as a function of reduced chemical potential for finite lattices with lengths $N = 2, 4, 6, 8$.

one-dimensional. In previous publications,^{19,20} we have considered two-dimensional adsorption compression on a uniform surface. Different dimensionalities result in important differences in the adsorption isotherms. However, the general pattern of adsorption behavior for repulsive molecules is the same: saturation at a reduced capacity and, then, growing to absolute capacity at much higher chemical potentials.

Note that the classical lattice mean-field chemical potential

$$\frac{\mu_s}{kT} = \ln \frac{\rho}{1-\rho} + \frac{z^* \epsilon}{kT} \rho \quad (17)$$

predicts two-dimensional condensation for attractive ϵ (with z^* being coordination number in the monolayer). However, changing the sign of ϵ to be repulsive in the expression for the classical mean-field chemical potential does not lead to adsorption compression. Strong repulsions result in a checkerboard structure at intermediate saturation (at half of the capacity, see Figure 2 for $\epsilon/kT = 9$), but mean-field averaging prevents the checkerboard structure and suppresses the adsorption compression phenomenon.

Finite Size Lattice

Real systems modeled by lattice theory are always finite and small systems are especially important because of interest in nanotechnology. In this section, we consider finite-size, one-dimensional lattices where the exact grand canonical partition function defined by (15) with (10), (12), and (14). Figure 3 shows the surface density as a function of chemical potential for $\epsilon/kT = 9$ with even lattice lengths with $N = 2, 4, 6, 8$. Figure 4 shows the same graph for odd lattice lengths with $N = 3, 5, 7$. As seen from Figures 3 and 4, at small N , the behavior of the system depends dramatically on N and there is a significant difference in the behavior of odd and even numbers of sites, N . Figure 5 illustrates that the difference between even and odd lattice sites still is noticeable for values of $N = 20$ and 21. Odd values of N give a much steeper step with inflection at $\rho = 1/2 + 1/2N$. Even values of N gives the first step at exactly $\rho = 1/2$ and an additional oscillation with inflection at $\rho = 1/2 + 1/N$.

The difference in density between the even and odd lattice arises from differences in structures of the adsorbed phase. For an odd number of lattice sites, the step occurs when molecules occupy alternating lattice sites with both endpoints are occupied. For the adsorption of additional molecules, all remaining lattice sites have equivalent energies resulting in a smooth transition to full capacity. For a lattice with an even number of sites, the first step occurs when half the lattice sites are filled with

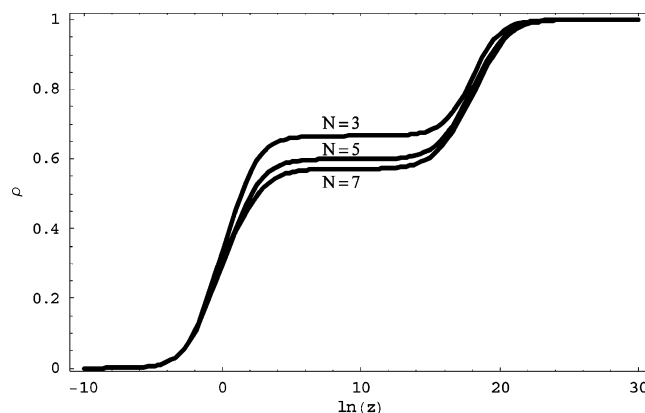


Figure 4. Adsorbed density as a function of reduced chemical potential with lattice parameters $N = 3, 5, 7$.

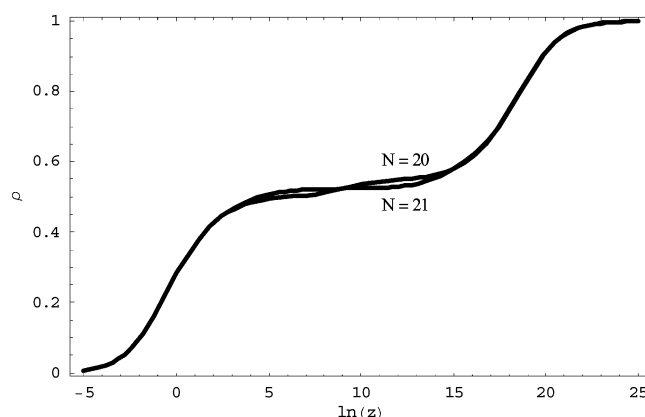


Figure 5. Adsorbed density as a function of reduced chemical potential with lattice parameters $N = 20$ and 21.

adsorbed molecules occupying alternating adsorption sites. For the adsorption of an additional molecule, there is a single site with only one nearest neighbor; all other adsorption sites have two nearest neighbor interactions. This difference in adsorption sites results in another step in the isotherm, after which the isotherm shows a smooth transition to full capacity. The differences for the odd and even number of lattice sites decrease as $1/N$ and converge to eq 14 in the thermodynamic limit.

Oscillations and Substeps in Experimental Isotherms

As illustrated in Figures 2–5, repulsive interactions between adsorbate molecules on a lattice can result in oscillations and substeps in the adsorption isotherm. Oscillations and steps have been observed in adsorption isotherms for various high-resolution measurements.^{42,43} In particular, oscillations in the isotherm have been observed for nitrogen on activated carbon⁴⁴ and for argon and nitrogen on heterogeneous carbosils in the range of low pressures.⁴⁵

High-resolution measurements have shown the existence of substeps for various ranges of density in submonolayer coverages. In particular, substeps at high densities have been observed for krypton, xenon, and argon on graphite, oxides and chlorides,^{46,47} and for xenon on cobalt chloride, nickel chloride, and silochrom at intermediate densities. Figure 6 illustrates classical substeps on magnesium oxide.

There has been much discussion on the nature of the substep for experimental isotherms.⁴ It commonly is believed that the substep represents a first-order transition between two-dimensional liquid and solid phases.⁴⁶ However, the nature of phase transitions for two-dimensional systems is not well

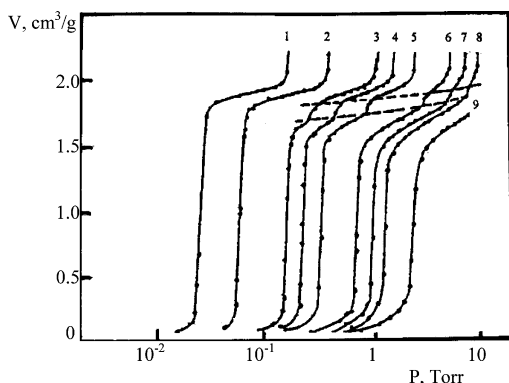


Figure 6. Substeps in adsorption isotherms for xenon on magnesium oxide at various temperatures. Data from ref 46.

understood even for the simplest case of hard sphere molecules.⁴⁸ Phase transitions on real surfaces are more complex than those of two-dimensional fluids because the atomic structure of the surface imposes structure on the adsorbed layer.

Conclusions

The adsorption of repulsive molecules shows important features that have not been analyzed in detail previously. The Langmuir adsorption model has been extended using the exact solution of the one-dimensional lattice to study the effects of repulsive interactions between adsorbate molecules at various confinements. This extension predicts a step in the isotherm for submonolayer coverage that has never been observed for lattice systems. This substep demonstrates that the phenomena of adsorption compression can be observed in lattice systems. Simultaneous occupation of these sites results in intermolecular repulsions between nearest neighbors. Hence, the adsorbed density on a surface can be much greater than that expected from the bulk fluid.

The substep in the lattice model with repulsive nearest neighbors is similar to substeps observed in a variety experimental systems. Nearest neighbor repulsions could provide a possible mechanism for this substep, along with known factors including surface heterogeneity.

Finite size has interesting effects on the shape of the adsorption isotherm. For strongly repulsive interactions, the shape of the isotherm for finite systems is fundamentally different for lattices with even or odd number of lattice sites. These finite size effects can produce additional steps in the adsorption isotherm that are lost only when examining the system at the thermodynamic limit.

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