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Stepwise Adsorption in Gas-Solid Adsorption System and Phase Transition in Adsorbed Phase

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In this work we have studied the multilayer stepwise adsorption of gases on solid adsorbents based on the previously developed theory. It is shown that stepwise adsorption isotherms emerge from our theory if an *ad hoc* adsorption regarding the degree of occupation for each successive layer is abolished and the effect of lateral intermolecular interactions among adsorbate molecules is included. In addition to these the effect of vertical interactions has also been taken into consideration. It seems that the vertical interaction plays a role in deciding the shape and the position of steps in resulting isotherms. It is evident from this research that it is the lateral interaction that is responsible for stepwise adsorption as long as the adsorbent surface is uniform and temperature is sufficiently low.

Introduction

Since its first appearance, the BET theory¹ has been playing the role of backbone in the study of multilayer physical adsorption of gases on solid adsorbents. The underlying model that characterizes this theory is mathematically so simple that it is still quite popular among many experimentalists. The parameters involved in this theory could successfully be interpreted in terms of physical quantities such as the monolayer capacity, the heat of condensation, *etc.* Unfortunately, however, it turned out that such a simple model itself could not explain many experimentally observed adsorption isotherms satisfactorily over interesting range of pressure and temperature. Many attempts have been made to improve the practical versatility of BET theory including the effect of intermolecular interactions among adsorbate molecules²⁻²⁰. Despite such efforts a universal model that could account for the observed isotherms over wide range of pressure and temperature has failed to emerge.

In a series of recent publications²¹⁻²⁴ Chang and his coworkers have proposed an interesting model that can correct many drawbacks of the BET theory while maintaining

the mathematical simplicity of the BET model itself. They have expressed a view that among so many things the piling pattern of molecules in the adsorbed phase is of leading importance. They have suggested that when multilayer adsorption occurs a molecule in the second or higher layer would more likely be adsorbed above the center of a square or triangular cluster of molecules, rather than on top of molecules themselves as assumed in the BET theory, in the underneath layer. Based on this view, Chang *et al.* could enumerate the number of adsorption sites available to the molecules in each successive layer and successfully derived better fitting isotherms. Thus it can be seen that if a minute modification regarding the molecular packing pattern in the adsorbed phase is introduced into the BET model a great improvement is gained over the original BET theory toward the desirable direction. In this manner Chang and his collaborators have paved a way that may lead to a better understanding of multilayer physical adsorption of gases on uniform solid surfaces.

One problem that has yet to be interpreted in terms of the Chang-Pak-Lee theory (henceforth referred to as the CPL theory) is the phenomena of stepwise adsorption.

The stepwise adsorption phenomena were much earlier predicted by Halsey²⁵ and Hill²⁶ and later were studied by many others²⁷⁻³². Nowadays it is well understood that sufficiently low temperature, uniform adsorbent surfaces, and lateral intermolecular interactions among adsorbate molecules are required for stepwise adsorption isotherms to be obtained. In a previous paper²³ Chang and his collaborators have modified their original theory introducing the effect of lateral interactions among the adsorbed molecules, but the resulting isotherms have failed to give the stepwise curves. They have closely examined the cause of such failure and have concluded that an *ad hoc* assumption introduced into their original theory was responsible for stepless isotherms. Thus we have decided to discard this assumption. Moreover, we introduce the effect of vertical interactions between the adsorbent surface and the adsorbed molecules as well as that of lateral interactions. In this paper it is shown that stepwise isotherms can emerge from the CPL theory when the lateral interactions are taken into account within the frame of Bragg-Williams approximation. It appears that the positions and shapes of steps in theoretical isotherms depend on the strength of lateral and vertical interactions in a complicated manner.

Theory

As in our previous work²¹, the number of adsorption sites available to the i -th layer molecules, M_i , may be written as

$$M_i = N_{i-1} (N_{i-1} / M_{i-1})^{n-1} \quad (1)$$

where N_{i-1} and M_{i-1} are, respectively, the number of molecules in the $(i-1)$ th layer and the number of sites available to these molecules, and n is a parameter to signify the piling pattern of adsorbed molecules.

The ratio N_i / M_i represents the degree of occupation for the i -th layer and will hereafter be denoted by x_i ; that is,

$$x_i = N_i / M_i \quad (2)$$

As in our previous work²⁴, we assume that the degree of occupation is same for all the layers beyond the k -th layer; that is,

$$x_{k+1} = x_{k+2} = \dots \equiv y \quad (3)$$

Then, in accordance with our previous work²⁴ the adsorption isotherm may be expressed as following:

$$\begin{aligned} \omega &= \sum_{i=1}^{\infty} N_i / M \\ &= x_1 + x_1^n x_2 + \dots + x_1^n x_2^n \dots x_{k-1}^n x_k \\ &\quad + (x_1^n x_2^n \dots x_k^n y) / (1 - y^n) \end{aligned} \quad (4)$$

where M is the number of adsorption sites and ω the average number of adsorbed molecules per adsorption site. The canonical partition function for the i -th layer molecules is given in the Bragg-Williams approximation as follows:

$$\begin{aligned} Q_i(M_i, N_i, T) \\ = \frac{M_i!}{(M_i - N_i)! N_i!} [q_i(T) \exp(-cWx_i/2kT)]^{N_i} \end{aligned} \quad (5)$$

where $q_i(T)$ is the average molecular partition function for

an i -th layer molecule in the absence of lateral intermolecular interactions, and c and W , respectively, represent the number of nearest sites around an adsorbed molecule in a two-dimensional adsorbed layer and the lateral interaction energy between a nearest neighboring pair of adsorbed molecules. k and T are, as usual, the Boltzmann constant and the absolute temperature of the system, respectively. Then, the canonical partition function for the entire adsorbed phase, Q , is approximately written as

$$Q = \prod_{i=1}^{\infty} Q_i(M_i, N_i, T) \quad (6)$$

In addition to Eq. (3) it is natural to assume that

$$q_1 \approx q_2 \approx \dots \approx q_k \approx q_{k+1} = \dots \equiv q \quad (7)$$

Note that $q_i(T)$ is in general a function of temperature T . Taking the logarithm of Eq. (6) and using the Stirling approximation, we have

$$\begin{aligned} M^{-1} \ln Q \\ = (x_1 - 1) \ln(1 - x_1) - x_1 \ln x_1 + x_1 \ln q_1 - Bx_1^2 \\ + x_1^n \{ (x_2 - 1) \ln(1 - x_2) - x_2 \ln x_2 + x_2 \ln q_2 - Bx_2^2 \} \\ \vdots \\ + x_1^n \dots x_{k-1}^n \{ (x_k - 1) \ln(1 - x_k) - x_k \ln x_k + x_k \ln q_k - Bx_k^2 \} \\ + (x_1^n \dots x_k^n) / (1 - y) \{ (y - 1) \ln(1 - y) - y \ln y + y \ln q - By^2 \} \end{aligned}$$

where $B = cW/2kT$.

Then, the Helmholtz free energy for the adsorbed phase, A , can be given by

$$-A/MkT = M^{-1} \ln Q \equiv \phi \quad (9)$$

For convenience we introduce a quantity g_i defined by

$$g_i = (\partial \phi / \partial x_i)_{\omega, x_{j \neq i}} \quad (10)$$

Since the system has a minimum value of Helmholtz free energy at equilibrium under the condition of constant M and T , we have

$$g_i = 0 \quad (11)$$

at equilibrium.

As in our previous works, we introduce another thermodynamic quantity given by

$$\psi = -\mu_A/kT \quad (12)$$

where μ_A is the chemical potential for the adsorbed phase. In order to facilitate the calculation of ψ let us pay our attention to the following identity:

$$\begin{aligned} \psi = -\mu_A/kT &= (\partial \phi / \partial \omega)_{g_1, \dots, g_k} \\ &= (\partial \phi / \partial \omega)_{x_k} + (\partial \phi / \partial x_1)_{\omega, x_{j \neq 1}} (\partial x_1 / \partial \omega)_{g_1, \dots, g_k} + \dots \\ &\quad + (\partial \phi / \partial x_k)_{\omega, x_{j \neq k}} (\partial x_k / \partial \omega)_{g_1, \dots, g_k} \end{aligned} \quad (13)$$

At equilibrium the above quantity is equal to $(\partial \phi / \partial \omega)_{x_k}$ since the rest of the terms on the righthand side of Eq. (13) vanish [cf. Eq. (11)]. Thus we have

$$\begin{aligned} \psi_{\text{eq.}} &= -(\mu_A/kT)_{\text{eq.}} = (\partial \phi / \partial \omega)_{x_k} \\ &= (1 - Yy^{n-1}) \ln(1 - y) - \ln y + \ln q - (2 - Yy^n) By \end{aligned} \quad (14)$$

were $Y = n/1 + (n-1)y^n$.

If use is made of the fact that at equilibrium the chemical potential for the adsorbed phase is equal to that for the vapor phase. Eq. (14) may be rewritten as

$$(1 - Yy^{n-1}) \ln(1-y) - \ln y + \ln q - (2 - Yy^n)By = -\mu_g^\circ/kT - \ln \xi \quad (15)$$

where μ_g° is the standard chemical potential for the vapor phase and ξ means the relative pressure, p/p^0 .

Rearrangement of Eq. (15) leads to a more convenient form

$$y = a\xi / [a\xi + (1-y)^{Yy^{n-1}} \cdot \exp\{B(2y - Yy^{n+1})\}] \quad (16)$$

where $a = q \exp(\mu_g^\circ/kT)$.

The conditions $g_1=0, g_2=0, \dots, g_k=0$ give us a set of equations from which we can obtain x_1, x_2, \dots, x_k as in our previous works. A detailed procedure for derivation of these equations has already been described in a previous paper²⁴. From the conditions $g_i=0$ ($i=1, \dots, k$) the following set of hierarchy equations results:

$$x_k = a\xi \{a\xi + (q/q_k)(1-y)^{Yx_k^{n-1}} \cdot \exp\{B(2x_k - Yx_k^{n+1})\}\}^{-1} \quad (17)$$

and

$$x_i = a\xi \{a\xi + (q/q_i) \prod_{j=i+1}^k (1-x_j)^{s_{ij}} \cdot \exp(-Bs_{ij} x_j^2) \cdot (1-y)^{Y(1-n)^{k-i} t_{ik}} \cdot \exp\{B(2x_i - Y(1-n)^{k-i} t_{ik} y^2)\}\}^{-1} \quad (18)$$

where $1 \leq i \leq k-1$, $s_{ij} = \prod_{l=i}^{j-1} n(1-n)^{j-l-1} x^{(n-\delta_{li})}$, and $t_{ik} = \prod_{l=i}^k x^{(n-\delta_{li})}$ with δ_{li} being the Kronecker's delta.

Calculations and Results

To find theoretical isotherms we first calculate y from Eq. (16) by iterative method for a given set of values of n , a , and B . Thus obtained value of y is then substituted into Eq. (17) and the iterative method is used again to calculate x_k for a given set of a , n , and q/q_k . The values of y and x_k obtained in this manner are then substituted into the equation for x_i and again use is made of the iterative method to find x_i for a given set of a , n , B , q/q_i , and k . Such process can be repeated until all the solutions for y , x_k, x_{k-1}, \dots, x_1 are found. Finally, thus obtained values are then substituted into Eq. (4) to find ω .

Figure. 1 through Figure. 3 illustrate that if we treat q/q_i as adjustable parameters the observed isotherms can nicely be fitted into the predicted theoretical isotherms. In all of these three cases we have set $k=3, n=3$, and $a=1$. In the region $\xi > 0.8$ the observed data show deviation from the predicted curves; however, as we have indicated in our previous work²², this may be due to the fact that a has been set equal to 1 for ease of calculation. a , by its definition [cf. Eq. (16)], can be close but never equal to 1. Thus one may expect that the aforementioned deviation in the regions $\xi > 0.8$ can be corrected by slight adjustment of a . We also have to emphasize that even though we treat here the

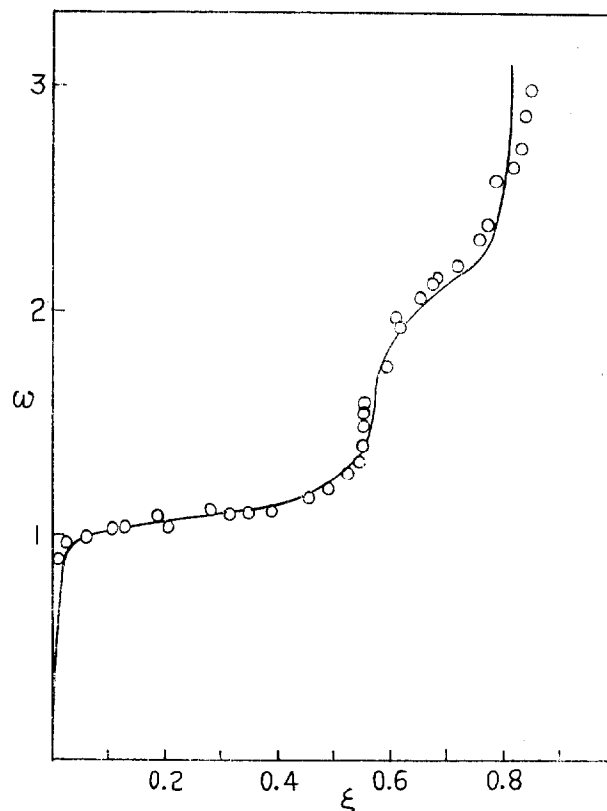


Figure 1. Comparison of the experimental and the calculated adsorption isotherm of ethyl chloride adsorbed on MTg at 184.3 °K. Circles; observed. Solid line; calculated ($B = -1.60, q/q_1 = 0.01, q/q_2 = 0.69, q/q_3 = 0.95$).

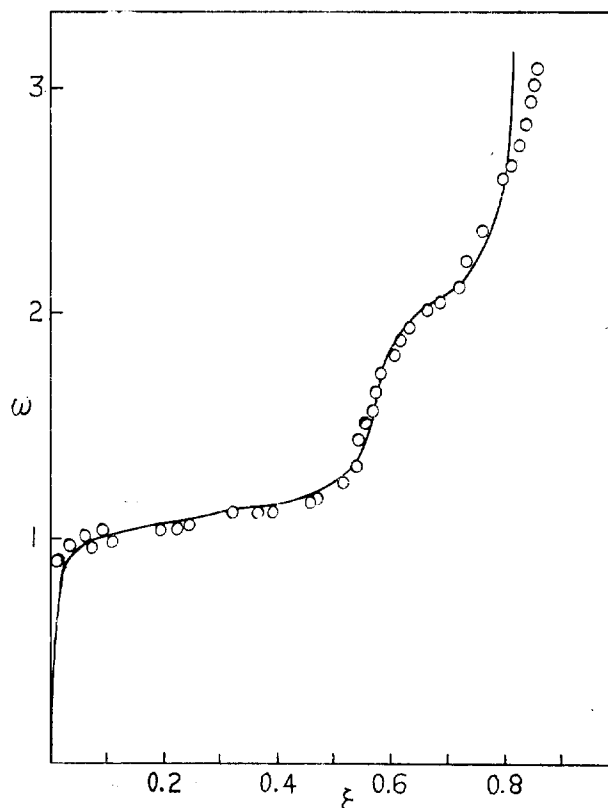


Figure 2. Comparison of the experimental and the calculated adsorption isotherm of ethyl chloride adsorbed on MTg at 195.5 °K. Circles; observed. Solid line; calculated ($B = -1.55, q/q_1 = 0.01, q/q_2 = 0.69, q/q_3 = 0.95$).

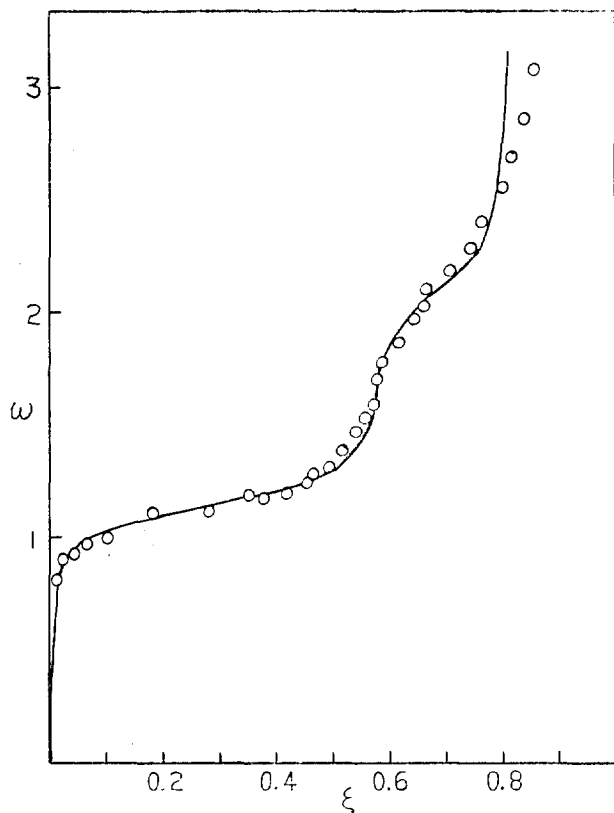


Figure 3. Comparison of the experimental and the calculated adsorption isotherm of ethyl chloride adsorbed on MTg at 210.1° K. Circles; observed. Solid line; calculated ($B = -1.50$, $q/q_1 = 0.01$, $q/q_2 = 0.69$, $q/q_3 = 0.95$).

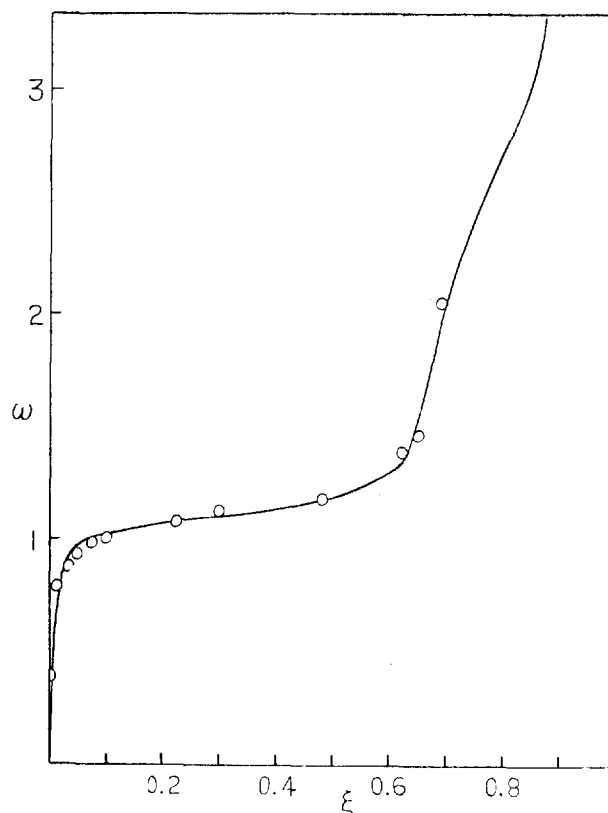


Figure 5. Comparison of the experimental and the calculated adsorption isotherm of cyclohexane adsorbed on Sterling MT at 263° K. Circles; observed. Solid line; calculated ($B = -1.55$, $q/q_1 = 0.01$, $q/q_2 = 0.78$, $q/q_3 = 0.96$).

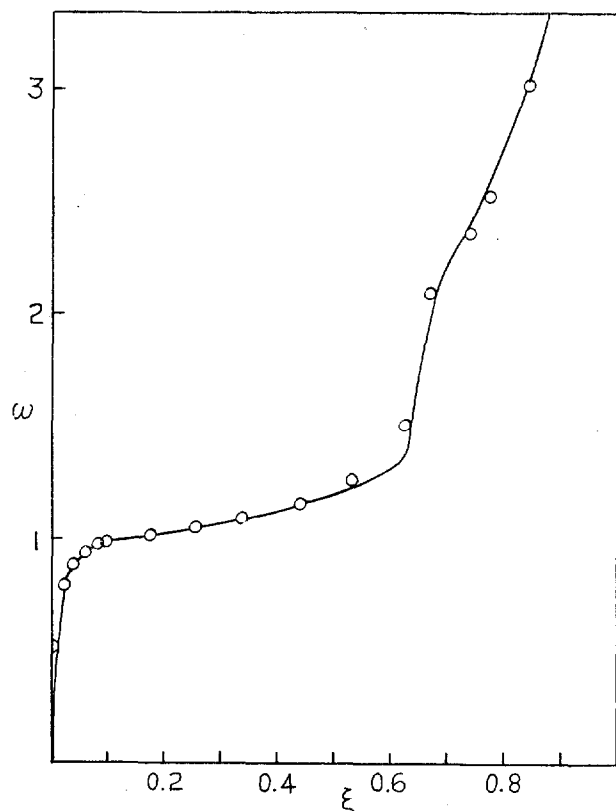


Figure 4. Comparison of the experimental and the calculated adsorption isotherm of cyclohexane adsorbed on Sterling MT at 253° K. Circles; observed. Solid line; calculated ($B = -1.65$, $q/q_1 = 0.01$, $q/q_2 = 0.78$, $q/q_3 = 0.96$).

quantities such as q/q_i , a , etc. as parameters they are not the parameters in a true sense. No doubt they are related to molecular motions and intermolecular interactions in one way or another; however, such relationships are completely unknown for the present. All we can do at this moment is to treat them as if they were parameters adjustable over certain ranges. Figure 4 and Figure 5 present another examples which show such treatment is indeed adequate.

In order to study the effect of temperature and vertical interactions consistently one must give the quantities q/q_i as a function of both temperature and vertical interaction energy the exact form of which is not known. At least qualitatively, however, this can be done by introducing a simple assumption. To do so we take out the term containing the vertical interaction energy from the molecular partition function. Thus one may approximately write

$$q_i = q_i^0 \exp(\epsilon_i/kT) \quad (19)$$

where ϵ_i is the vertical interaction energy of a molecule in the i -th layer and q_i^0 is the part of molecular partition function that is almost independent of the variation of ϵ_i . As in our previous work, ϵ_i can be divided into two parts. The first part is the interaction of the adsorbed molecule with the surface of adsorbent and this interaction energy may be assumed to vary as r^{-3} where r is the distance from the adsorbent surface³³. The second part is the interaction of the molecule with other molecules in the neighboring layers. Although the latter interaction may show the layer

by layer variation depending on the degree of occupation for each layer, we will simply assume that they are constant throughout the adsorbed phase except for the first layer and this energy will be denoted by ϵ . Then, ϵ_i 's may in general be expressed as

$$\epsilon_i = \epsilon + (\epsilon_1 - \epsilon) \left\{ \frac{\delta}{\delta + (i-1)d} \right\}^3 \quad (20)$$

where ϵ_1 is the average vertical interaction energy between a first-layer molecule and the adsorbent surface and δ and d are, respectively, the distance between the first layer and the solid surface and the separation between two successive layers. From Eqs. (19) and (20) we have

$$q/q_i = \exp\left[-(\epsilon - \epsilon_1) \left\{ 1 + (i-1) \left(\frac{d}{\delta} \right) \right\}^{-3} / kT\right] \quad (21)$$

In this manner we can express all the q/q_i 's in terms of two parameters ϵ_1 and d/δ . Eq. (21) can be substituted into Eqs. (17) and (18) and x_i may be calculated for a given set of a , n , k , B , ϵ_1 , and d/δ . In view of the results obtained previously n may normally be set equal to 3. Figure 6 through Figure 14 demonstrate the results obtained for various sets of ϵ_1 , d/δ , and $cW/2$. Figure 8, in particular, tells us that it is the lateral intermolecular interactions among adsorbate molecules that are responsible for the stepwise isotherms. From Figure 8 we can also see that steps in the isotherms gradually disappear as lateral interactions get weaker, and as we have already seen in our previous work, these steps completely smooth out in the limit of no lateral interactions.

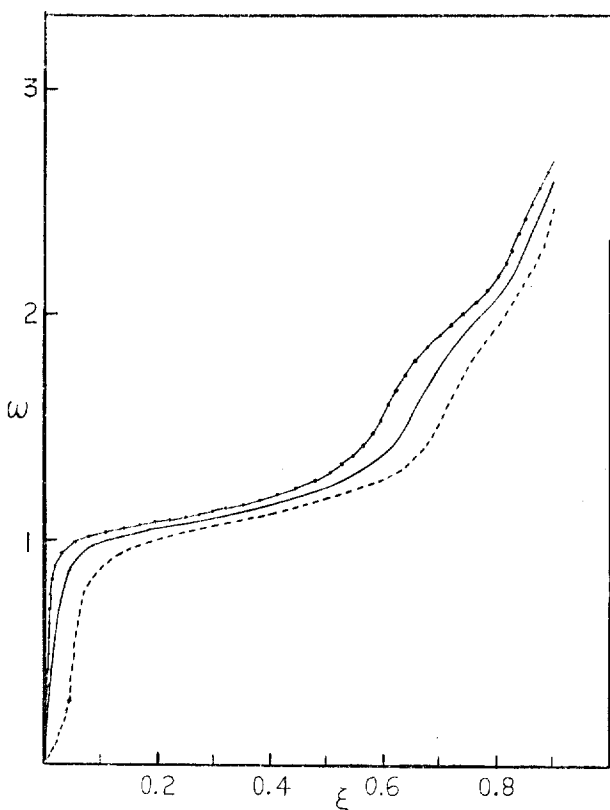


Figure 6. The calculated adsorption isotherm at 200° K. ($\epsilon = -4.40 \times 10^{-13}$ erg, $cW/2 = -4.20 \times 10^{-14}$ erg, $d/\delta = 1.16$, $a = 0.20$) Upper dotted solid line; for $\epsilon_1 = -5.25 \times 10^{-13}$ erg. Middle solid line; for $\epsilon_1 = -5.50 \times 10^{-13}$ erg. Lower broken line; for $\epsilon_1 = -5.75 \times 10^{-13}$ erg.

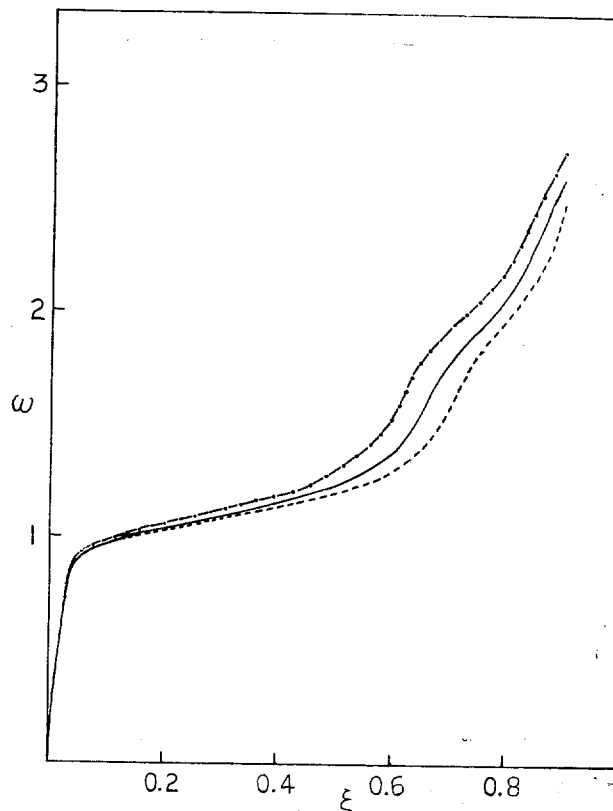


Figure 7. The calculated adsorption isotherm at 200° K. ($\epsilon = -4.40 \times 10^{-13}$ erg, $\epsilon_1 = -5.50 \times 10^{-13}$ erg, $cW/2 = -4.20 \times 10^{-14}$ erg, $a = 0.20$). Upper dotted solid line; for $d/\delta = 1.32$. Middle solid line; for $d/\delta = 1.16$. Lower broken line; for $d/\delta = 1.00$.

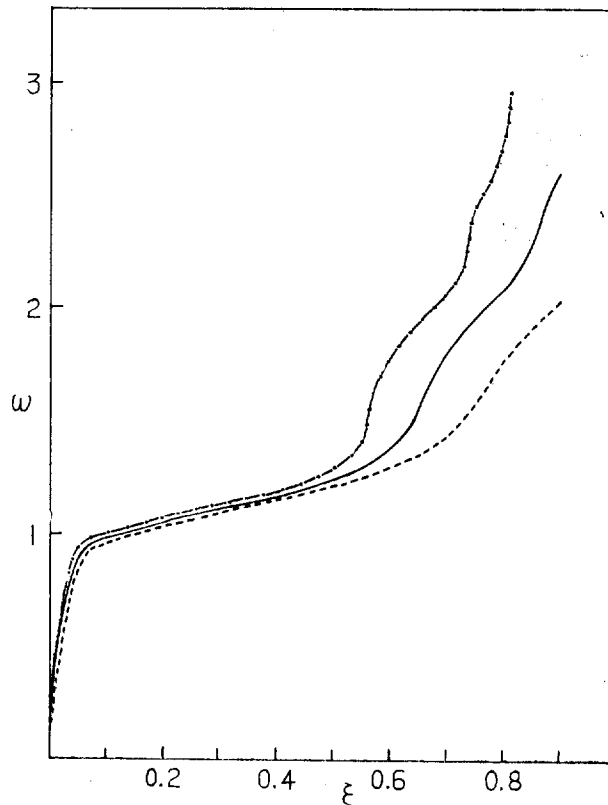


Figure 8. The calculated adsorption isotherm at 200° K. ($\epsilon = -4.40 \times 10^{-13}$ erg, $\epsilon_1 = -5.50 \times 10^{-13}$ erg, $d/\delta = 1.16$, $a = 0.20$). Upper dotted solid line; for $cW/2 = -3.80 \times 10^{-14}$ erg. Middle solid line; for $cW/2 = -4.20 \times 10^{-14}$ erg. Lower broken line; for $cW/2 = -4.60 \times 10^{-14}$ erg.

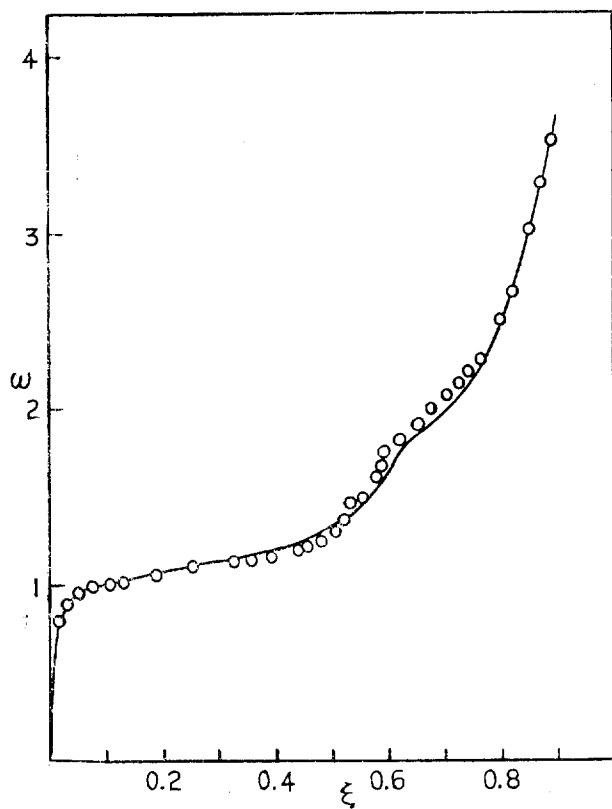


Figure 9. The adsorption isotherm of ethyl chloride adsorbed on MTg at 210° K. Circles; observed. Solid line; calculated ($\epsilon = -4.38 \times 10^{-13}$ erg, $\epsilon_1 = -5.64 \times 10^{-13}$ erg, $cW/2 = -4.18 \times 10^{-14}$ erg, $d/\delta = 1.17$, $a = 0.23$).

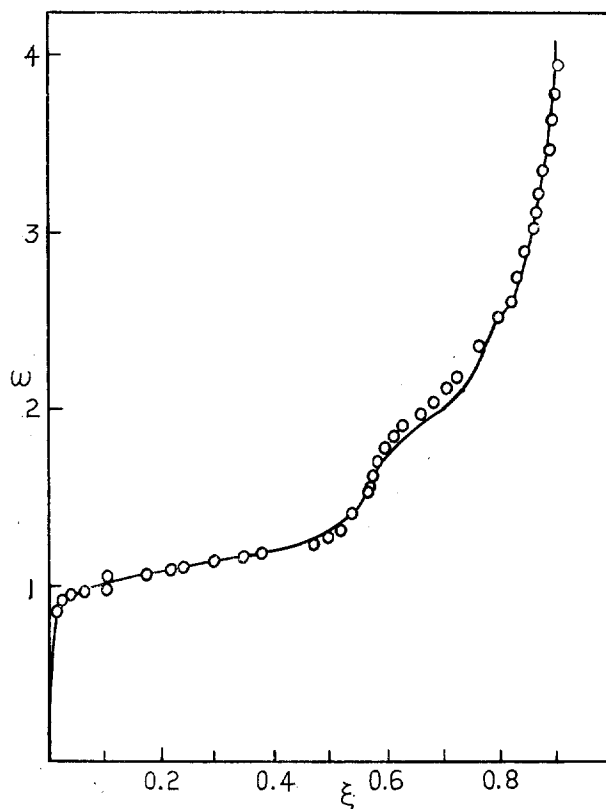


Figure 11. The adsorption isotherm of ethyl chloride adsorbed on MTg at 184° K. Circles; observed. Solid line; calculated ($\epsilon = -4.38 \times 10^{-13}$ erg, $\epsilon_1 = -5.64 \times 10^{-13}$ erg, $cW/2 = -4.18 \times 10^{-14}$ erg, $d/\delta = 1.17$, $a = 0.19$).

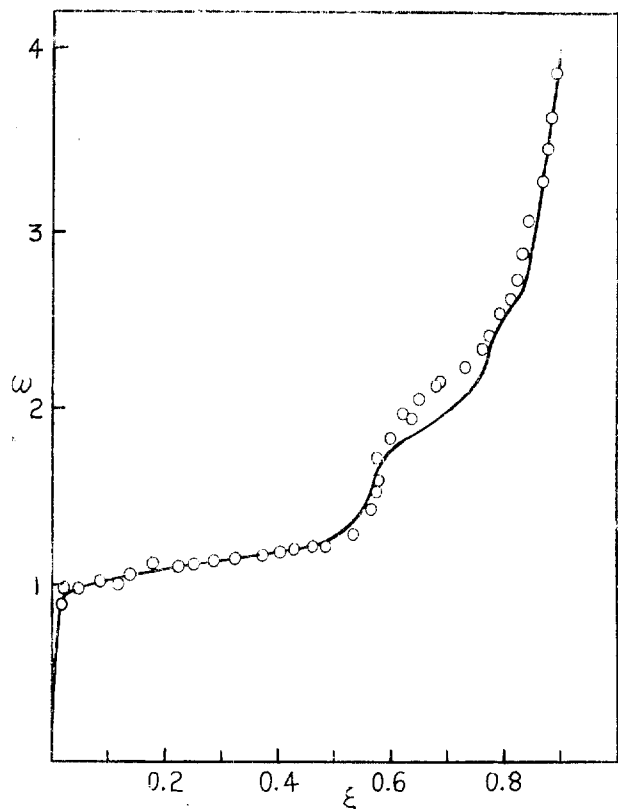


Figure 10. The adsorption isotherm of ethyl chloride adsorbed on MTg at 195° K. Circles; observed. Solid line; calculated ($\epsilon = -4.38 \times 10^{-13}$ erg, $\epsilon_1 = -5.64 \times 10^{-13}$ erg, $cW/2 = -4.18 \times 10^{-14}$ erg, $d/\delta = 1.17$, $a = 0.21$).

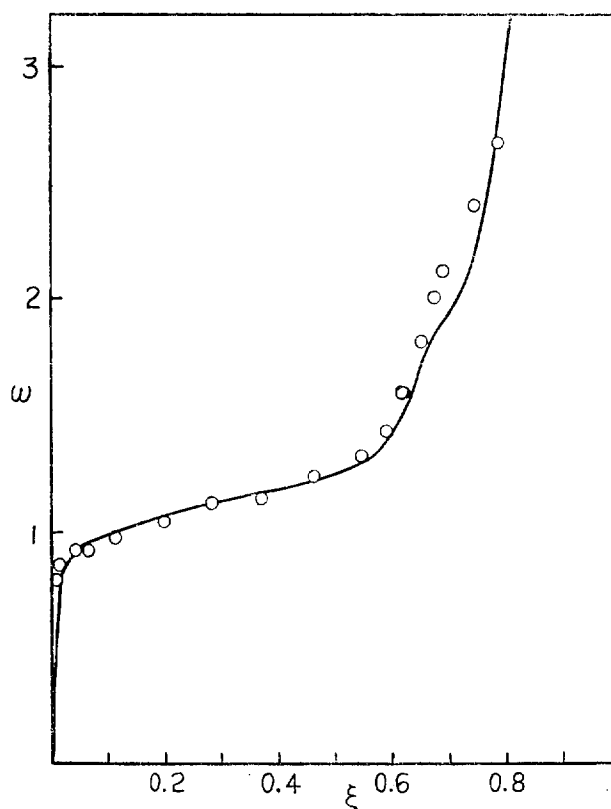


Figure 12. The adsorption isotherm of cyclohexane adsorbed on Sterling MT at 273° K. Circles; observed. Solid line; calculated ($\epsilon = -5.44 \times 10^{-13}$ erg, $\epsilon_1 = -6.93 \times 10^{-13}$ erg, $cW/2 = -5.81 \times 10^{-14}$ erg, $d/\delta = 1.53$, $a = 0.23$).

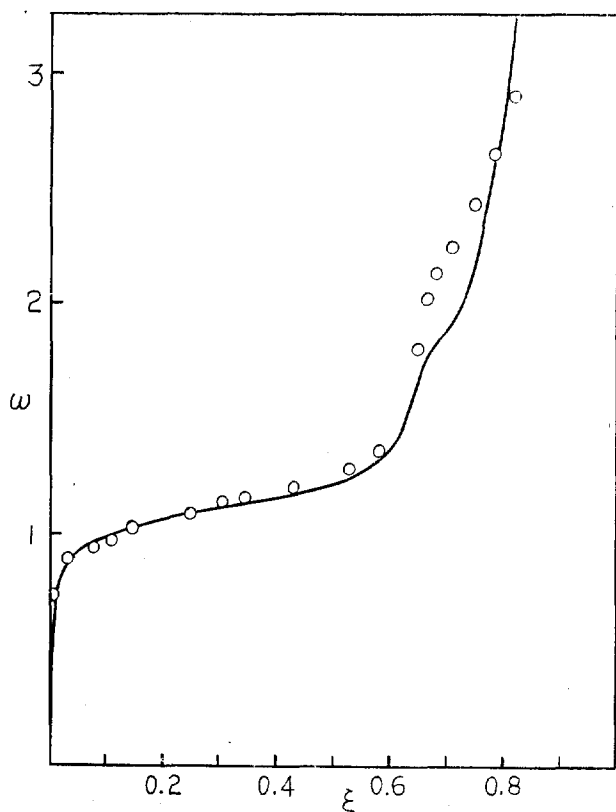


Figure 13. The adsorption isotherm of cyclohexane adsorbed on Sterling MT at 263 °K. Circles; observed. Solid line; calculated ($\epsilon = -5.44 \times 10^{-13}$ erg, $\epsilon_1 = -6.93 \times 10^{-13}$ erg, $cW/2 = -5.81 \times 10^{-14}$ erg, $d/\delta = 1.53$, $a = 0.22$).

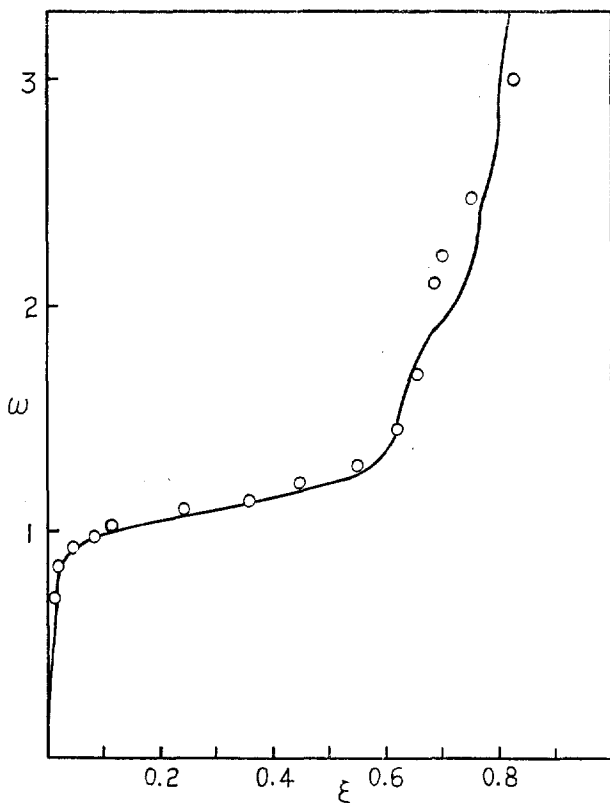


Figure 14. The adsorption isotherm of cyclohexane adsorbed on Sterling MT at 253 °K. Circles; observed. Solid line; calculated ($\epsilon = -5.44 \times 10^{-13}$ erg, $\epsilon_1 = -6.93 \times 10^{-13}$ erg, $cW/2 = -5.81 \times 10^{-14}$ erg, $d/\delta = 1.53$, $a = 0.20$).

Thus we may say that weakening of lateral interactions makes steps in adsorption isotherms less conspicuous whatever the causes may be, be it nonuniformity of the adsorbent surface or thermal motions of adsorbate molecules.

Nonuniformity of the adsorbent surface prevents the ordered packing of adsorbate molecules and high temperature induces vigorous thermal motions of the molecules, thus reducing the effect of lateral interactions. To illustrate this point we intend to measure the amount of adsorption of cyclohexane and benzene on a graphitized carbon black called the Sterling MT, and the experiment is under way in our laboratory. The results will be published in a subsequent paper.

Conclusion and Discussion

From the results of this research a few conclusions may be drawn. First, it is confirmed that the CPL theory can provide a sound basis for studying the stepwise adsorption when the effect of lateral and vertical interactions is introduced into it. Secondly, it can be concluded that it is the lateral intermolecular interactions among adsorbate molecules that is responsible for stepwise adsorption and that any factor which can lessen the effect of such interactions make the steps in adsorption isotherms disappear partly or completely. Thirdly, although the vertical interaction itself does not affect the shape of steps directly, it appears that it has some influences upon the position of step in the isotherm as we can see from Figure 6. Furthermore, it is conceivable that the vertical interaction also affects the effectiveness of lateral interaction by restricting thermal motions of adsorbed molecules.

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Molecular Dynamic Study of a Polymeric Solution (I). Chain-Length Effect

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Dynamic and equilibrium structures of a polymer chain immersed in solvent molecules have been investigated by a molecular dynamic method. The calculation employs the Lennard-Jones potential function to represent the interactions between two solvent molecules (SS) and between a constituent particle (monomer unit) of the polymer chain and a solvent molecule (CS) as well as between two non-nearest neighbor constituent particles of the polymer chain (CC), while the chemical bond for nearest neighbor constituent particles was chosen to follow a harmonic oscillator potential law. The correlation function for the SS, CS and CC pairs, the end-to-end distance square and the radius of gyration square were calculated by varying the chain length (=5, 10, 15, 20). The computed end-to-end distance square and the radius of gyration square were found to be in a fairly good agreement with the corresponding results from the random-flight model. Unlike earlier works, the present simulation result shows that the autocorrelation function of the radius of gyration square decays slower than that of the end-to-end distance square.

Introduction

Polymers have several properties (viscosity, dielectric relaxation, *etc.*) which are distinctly different from those of monomers and low molecular weight compounds. The molecular weight of a polymer may be varied almost continuously from low to high by changing the degree of polymerization. Moreover, an individual polymer molecule has nearly infinite conformations. Therefore, it is difficult to derive physical properties of polymer systems from an *ab initio* theory.

Recent development of high-speed and high-capacity computers makes it possible to study complicated systems such as polymeric systems. Several attempts have been made in the past to simulate polymeric systems. The simulations on polymeric systems may be done either by the Monte Carlo method¹⁻⁹ or by the molecular dynamic method.¹⁰⁻¹²

In Verdier's Monte Carlo simulation,⁷⁻⁹ a polymer molecule was represented by a chain of connected lattice points, the unconnected lattice points by the solvent molecules. The constituent particles (or atoms) of the polymer chain have to be moved to other lattice points by a kinetic rule. It has been, however, pointed out that the Verdier's result may depend on the specific model used.^{13,14} Ceperly and Kalos¹⁵ simulated the dynamics of a polymer chain immersed in solvent, subject to both internal polymer force and random fluctuating solvent force. The simulation was done by solving the Smoluchowski equation for the time-evolution of the polymer probability density. The Smoluchowski equation does not take into account the solvent structure and solute-solvent interaction. Such details may greatly influence the dynamics of the polymer. The present study was undertaken to examine the behavior of the polymer in solution by carrying out the molecular dynamic calculation,