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ABSTRACT

To study the ordering of molecules adsorbed on single-crystal substrates, a molecular cross-section (MCS) is defined, which measures the surface area occupied by each molecule. With this MCS, a two-dimensional packing coefficient C_{2D} is then defined for ordered arrays of adsorbed molecules. Values and trends for MCS and C_{2D} are discussed for known surface structures, especially for benzene adsorbed on metal surfaces. The packing is found to be generally less dense at surfaces than one would expect from comparison with packing in three-dimensional organic crystals. The Van der Waals packing energy and the repulsive dipole-dipole energy are also computed to study this issue. The lack of close-packing is attributed to the need to respect structural coincidence with the substrate and/or co-adsorption of small molecules like CO. These concepts are then applied to the prediction of the long-range order that a monolayer of adsorbed molecules may adopt: thereby possible adsorption structures can be defined, restricting the number of possibilities in a further structural determination.

1. Introduction

Monolayers of molecules adsorbed on metal single-crystal surfaces very often adopt ordered structures, as evidenced by Low-Energy Electron Diffraction (LEED) patterns.[1] The ordering of adsorbates is governed by both "direct" adsorbate-adsorbate interactions (such as Van der Waals and dipole-dipole forces), and by "indirect" interactions which involve the substrate.[2]

To examine the relative importance of these interactions, we have investigated to what extent the "direct" adsorbate-adsorbate interactions can explain the observations, by focussing our attention on Van der Waals and dipole-dipole interactions among adsorbed molecules. We have previously studied[3] Van der Waals interactions in monolayers, by the usual summations of organic lattice theories.[4]

To that end, we also define the even simpler concepts of the area occupied by an adsorbed molecule (molecular cross-section or MCS) and the two-dimensional packing coefficient C_{2D}, which can be compared with the corresponding quantity in the many well-known three-dimensional organic crystals. We find that the observed packing coefficients are generally smaller than the ideal closest-packing value. This discrepancy is not attributable to the repulsive dipole-dipole interactions, but rather to the requirement of commensurability or structural coincidence with the substrate.

These concepts are then used to predict possible ordered structures for adsorbed molecules. Our results show that many observed structures can be predicted on the basis of Van der Waals forces and commensurability,

while dipole-dipole interactions would only play a role with loosely-packed molecules that have a large dipole moment perpendicular to the surface. Some other structures that are detected by LEED cannot be explained by our calculations, unless co-adsorption of other molecules (e.g. CO) is assumed.

2. The Model

2.1 Molecular Cross-Section (MCS)

In order to obtain a packing coefficient in three-dimensional space, one has to know the molecular volume; the problem is now fully solved for three-dimensional molecular crystals.[5a] For a monolayer, one has to define a two-dimensional entity with which to argue by analogy: this entity we call molecular cross-section (MCS). It is the area included within the projection on a plane of all atomic spheres in a molecule, as sketched in Figure 1. It depends on the molecular geometry and the Van der Waals radii. It should not be confused with the effective molecular surface (or envelope) area, this being the exposed non-planar surface of a molecular object made up of intersecting atomic spheres.[5b]

Numerical data needed to compute the MCS are to be found in ref. [5a], as is the description of the numerical integration procedure. Its adaptation to two dimensions involves the sampling of an area, A, of the projection plane, enclosing the whole MCS, with N probe points (typically, 200 points per $Å^2$), N_I of which will fall inside the projection surface, or MCS. The area of this surface is then

$$A_S = A\, N_I / N$$

Note that the MCS is defined, whatever the final fate of the adsorbate, for the molecule in its conformation before adsorption. The MCS may be obtained with a computer, but a drawing on cardboard, followed by clipping and weighing the resulting figure, would do as well. Table 1 gives numerical values for the MCS, and Table 2 provides group increments for approximate MCS calculations for many molecules. This allows the MCS of more complex molecules to be calculated by simple addition of the projected areas of their constituent groups. For instance, the MCS of flat-lying fluorobenzene is obtained by adding the group increments for $-C_6H_5$ and $-F$, yielding $31.2 + 4.5 = 35.7 Å^2$.

The numerical value of the MCS is somewhat sensitive to the choice of the Van der Waals radii, much less so to small variations in bond lengths or molecular conformation, such as the orientation of C-H bonds in a CH_3 group. One can however be confident that the main conclusions about surface geometry that can be drawn from this model will survive minor changes in parametrization, especially for simple organic molecules, where the range of variation of these parameters is restricted. On the other hand, the overall molecular orientation with respect to the surface on which it is projected has to be carefully specified; many MCS values are possible for the same molecule. Our analysis and data in the present work refer mostly to simple cases, such as flat benzene or flat ethylene.

2.2 Two-Dimensional Packing Coefficient

The packing coefficient in two dimensions is the ratio of the area covered by adsorbed molecules to the total available area. In the case of a periodic adsorption structure, this can be evaluated as:

$$C_{2D} = \frac{Z \cdot MCS}{A_C}$$

where Z is the number of molecules in the surface unit cell of area A_C. This unit cell may be known from LEED patterns.

Suppose one calculates C_{2D} for a given molecule with an assumed adsorption orientation, using the unit cell area determined by LEED. What one learns at first sight from this C_{2D} is:

a) if $C_{2D} > 1$, adsorption must involve a different orientation, a conformational change, fragmentation or multilayer formation;

b) if C_{2D} is too small even though the surface has been exposed to saturation doses, the question arises of why the molecules would not (or could not) pack more closely on the surface.

To estimate what can be "too small", the following argument can be put forward. In three-dimensional organic crystals, an universal packing coefficient $C_{3D} \simeq 0.7$ applies.[4] This is quite near to the closest-packing coefficient for spheres in space (namely 0.7405). Organic crystal chemistry[4] offers a wide range of structures, from the low-temperature, high pressure phases for which C_{3D} may reach 0.77, to the rotationally or translationally unstable, plastic phases for which it drops to 0.65.

The corresponding quantity for circles on a surface is 0.907, so that this, by analogy, should be the close-packing coefficient to be observed for surface structures. For reference and comparison, Table 3 collects packing coefficients observed for two-dimensional structures at or near saturation coverage. Higher than ideal packing coefficients can be explained as above. However, many of these structures, as well as others (e.g. benzene, to be discussed in a later section), have less than the ideal closepacking coefficient of 0.907. The simplest explanation of such loose packing is the need to respect commensurability (ie. structural coincidence) of the overlayer with the substrate: the imposition of on-site binding to the substrate dominates the structure formation process. However, since on dense, highly regular metal surfaces many commensurate cells are possible for the adsorbate with the same surface binding site, we propose that packing considerations play a substantial role in the choice. Also, it must be remembered that the commensurability requirement imposes a discontinuous variation of overlayer cell edges, and thus prevents, generally speaking, the reaching of optimum packing coefficients.

2.3 Automatic Search for Possible Surface Cells

It is possible to consider the matter from the other end, i.e. one may ask which are the possible surface cells that produce close-packed structures, given the adsorbate MCS. With such predicted unit cells, one may then try to observe their existence experimentally. Failure to observe possible cells is a sign that other forces are active, besides the interadsorbate interactions. A computer program has been prepared to generate in a systematic way all possible cells on a (111), (110) or (100) surface of an fcc metal. The cells are assumed to have coincidence

with the substrate, as given by the familiar superlattice matrix of the general form $\begin{pmatrix} m & n \\ p & q \end{pmatrix}$, where the four components run from preset minimum to maximum values. (This matrix has the following meaning: if $\underline{a}_1$ and $\underline{a}_2$ are the (1x1) unit cell vectors of the substrate, then the ordered overlayer has a unit cell with basis vectors $\underline{b}_1 = m\underline{a}_1 + n\underline{a}_2$ and $\underline{b}_2 = p\underline{a}_1 + q\underline{a}_2$; note that the cell angle is chosen to be 120° on (111)). Further limitations can be imposed by setting minimum values for cell edges and angles, depending on the adsorbate MCS, and the condition $C_{min} < C_{2D} < 1$ is also imposed. Experience indicates $C_{min} = 0.4$ to 0.5 to be a reasonable value. We shall limit ourselves here to cases in which $Z = 1$; for $Z > 1$, i.e. more than one molecule per cell, another approach is perhaps more useful. If the MCS is other than roughly circular, then close-packing requires a symmetry other than purely translational, and the combined effects of translation and rotation must be accounted for.[2] The basic requirement, $C_{2D} < 1$, still holds, but contains less structural information. In a later section, we shall illustrate the automatic search for surface cells in the case of benzene on various metal surfaces.

2.4 Dipole-Dipole Energies

Overlayers have been observed, which are even less densely packed than allowed by commensurability with the substrate and predicted by close-packing. One plausible explanation for this is an electrostatic repulsion between the vertical, parallel dipoles of neighbouring adsorbed molecules; such dipoles are formed by the molecular dipole moment or by the surface-adsorbate charge transfer as well as by image dipoles.

The coulombic potential energy of such an array of dipoles is approximated by

$$E_C = \sum_j \frac{q^2}{\varepsilon} \frac{1}{4\pi\varepsilon_o} \frac{R^2}{D_j^3}$$

where q is the point charge, R is the dipole length, and D_j are the distances between a reference dipole and the surrounding ones. The dielectric constant of the medium, ε, is not known, while q values can sometimes be inferred from work function changes. For our order of magnitude calculations, however, the quantity q^2/ε has been treated as an adjustable constant, which takes care of the mutual depolarization of dipoles as well as of the effect of image charges (see refs. [4] and [13] for similar considerations in organic crystals, and ref. [14] for the nature and origin of surface dipoles). We shall calculate this dipole-dipole energy for benzene in the next section to estimate its importance.

3. Application: Intralayer Formation Energy for Benzene Adsorption

Benzene readily chemisorbs on a number of metal surfaces and a variety of ordered structures is found: Ni(100)-c(4x4),[15] Ni(111)-(2√3x2√3)R30°,[15] Ir(111)-(3x3),[16] Pd(100)-c(4x4),[17] Pt(111)-(2√3x4)rect,[18] Pt(111)-(2√3x5)rect,[18] Rh(111)-c(2√3x4)rect,[19] Rh(111)-(3x3),[19] Rh(111)-(√7x√7)R19.1°[2] and Rh(111)-(2√3x3)rect.[20]

A cell search for benzene on several of these metal surfaces has been conducted as described in Section 2.3. We used the limits: $0.4 < C_{2D} < 0.97$; m, n, p, q ≤ 5; minimum cell edge or diagonal, 7Å (approximately the diameter of the MCS for benzene). For each possible cell, then, the non-bonded (Van der Waals) potential energy has been computed as described in

previous work,[1-2] and the dipole-dipole energy as outlined in section 2.4, using $q = 0.1$ electrons, $\varepsilon = 1$, $R = 2.15$Å.

Overall results are reported in Table 4, while in Figure 2 the layer packing energies are plotted against the packing coefficient C_{2D}. For Rh(111), the structures which are most stable on packing grounds are those that have been observed experimentally, and the same is true for Ni(100). For Ni(111), the apparently very favourable (3x3) cell has not been observed to our knowledge, while a loosely packed 12x cell, $(2\sqrt{3}x2\sqrt{3})R30°$, does exist (Nx indicates a unit cell area N times that of the (1x1) cell). Our work suggests strongly that in favorable conditions (temperature, exposure) the (3x3) cell must be observable for benzene on Ni(111). In any case, Ni(111) is very different from Rh or Pt, in that all 7x, 8x, 10x or 11x cells are forbidden because one cell edge of 6.6Å is too short for benzene to fit flat.

Figure 2 gives an estimate of the relative importance of non-bonded and dipole-dipole energies. In these examples, the dipole-dipole energy, which is repulsive, does not seem to have sufficient strength to force the adoption of loosely packed structures, and seems to change much more slowly than the Van der Waals energy on changing the packing conditions. However, for more strongly polar molecules, the dipole-dipole energy might dominate in the loosely-packed structure, because of its larger range. In any case, the simple trends visible in Figure 2 can be used to obtain an estimate of the intralayer forces in any structure generated by aromatic molecules on metal surfaces.

The almost circular shape of the benzene MCS causes the intralayer rotational barrier to be very low, as is evident from our packing energy

calculations; in the closely-packed 7x structure on Rh(111) (see Table 4), the highest barrier is observed, namely 1.7 kcal/mole. The layer-surface interaction energy is however considerable and site-dependent, and its contribution to the barrier to the in-plane rotation of benzene might be larger. This matter is being considered in work in progress[21] by means of Extended Hückel calculations. Preliminary data show the barrier to be significant, although site-dependent.

When use is made of close-packing concepts to predict possible surface structures, it should be kept in mind that, all other things being equal, there apparently is a tendency to the formation of the most symmetrical surface cell by the adsorbate, as appears from careful inspection of Table 4 and of other similar data we have obtained. This points to a possibly relevant entropy contribution to the layer free energy.

Finally, let us consider some of the observed (but not fully elucidated) benzene structures reported on metals. On Pt(111) two cells have been found, labeled $(2\sqrt{3}x4)$rect and $(2\sqrt{3}x5)$rect,[19] which, even if occupied by two benzene molecules, are loosely packed. On Rh(111), the $(2\sqrt{3}x4)$rect structure has been successfully interpreted by LEED intensity analysis by dynamical scattering calculations,[19b] while the quite comparable (3x3) structure still defies efforts of interpretation. If the close-packing principle were obeyed ($C_{2D} \simeq 0.9$), one should conclude that the $(2\sqrt{3}x5)$rect Pt(111) benzene structure allows for 51Å^2 of extra space (almost the MCS of one additional benzene molecule), while the (3x3) structure on Rh(111) allows an extra 16Å^2.

In fact, in recent vibrational loss measurements have detected other co-adsorbed species, mainly CO, in several of these benzene adsorption systems;[22] the MCS for upright CO is simply that of the C atom, 9.62Å^2, so that up to 5 CO molecules may fit in the 51Å^2 of free cell space for the (2√3x5)rect structure. No doubt, Van der Waals interactions with such a small and mobile species could easily be optimized. The case is mentioned as a further example of possible applications of the close-packing principle on surfaces, in suggesting new structures such as co-adsorbed surface structures and testing them for intralayer stability. Further investigation of a reduced subset of surface structures may then proceed, coupled with other information, obtained from HREELS and dynamical LEED calculations.

4. Conclusions

Our main results regarding the effects of adsorbate-adsorbate interactions between organic molecules are as follows.

(1) The examination of the packing coefficients is most useful in studying molecular adsorption. If too high a packing density is found, one may have molecular tilting, a conformational change, fragmentation or multilayer formation. In examining a series of known structures, we have noticed a less than optimal packing density, which we attribute in general to the requirement of commensurability due to strong on-site bonding, and possibly to entropy effects favoring the most symmetrical structures.

(2) Some structures apparently exhibit even looser packing (e.g. benzene on Pt(111)). Repulsive dipole-dipole interactions do not account for this observation. While we have shown that the extra space is sufficiently large to accommodate other molecules, other explanations are possible. A serious candidate is through-substrate interactions, which

would have to range only a few atomic diameters through the metal. More extensive experimental tests of these and other systems are required to resolve this issue. In particular, it would be valuable to determine the phase diagram for these molecular adsorbates (this is delicate, because of chemical processes that can and do occur).

(3) The methods described here (use of molecular cross-section, packing density and Van der Waals interactions) are very useful in defining possible adsorption structures of molecules on metal surfaces. We have exhibited their application to undistorted molecules. They can easily be extended to distorted molecules and other chemical species. Such possible structures are very valuable input for more detailed structural determinations based on LEED intensity calculations.

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TABLE 1

Molecular cross sections (in $Å^2$) of molecules with their gas-phase geometry. All C-C bonds are chosen parallel to the projection surface unless otherwise stated.

Ethane	16.78
Fluoroethane	17.89
Chloroethane	21.72
Ethylene	17.84
Acetylene	15.54
Propane	21.89
Methylacetylene	20.60
Propene	23.02
Butadiene	29.09
Benzene	34.43
Toluene	39.58
Fluorobenzene	35.66
Chlorobenzene	39.39
Naphthalene	50.91
Methane,[a] or upright ethylidyne	12.02
Propylidyne[b]	17.71
Cyclohexane[c]	34.40

a) One C-H bond perpendicular to the surface.
b) C-CH_2 bond perpendicular to the surface, CH_2-CH_3 bond at 109.5° to surface normal.
c) Average molecular plane of C atoms parallel to the surface.

TABLE 2

Group increments ($Å^2$) for the calculation of molecular cross sections.

Fragment	Description	Group Increment
$-CH_3$	As in flat ethane	8.4
$>CH_2$	As in flat propane	5.1
$=CH_2$	As in flat ethylene	8.9
$\equiv CH$	As in horizontal acetylene	7.8
$-C\equiv CH$	Horizontal	12.2
$-CH=CH_2$	Flat	14.6
$-C_6H_5$	Flat	31.2
$-F$		4.5
$-Cl$		8.2
C (aromatic)		2.53
H (aromatic)		3.20

TABLE 3

Packing coefficients, C_{2D}, for layers of molecules adsorbed on metal surfaces.

Adsorbate	Surface	C_{2D}	Reference
Acetylene	(2x2)Pt(111)	0.583	[6]
Ethylene	(2x2)Pt(111)	0.670	[6]
	(2x2)Ni(111)	0.822	[7]
	c(4x2)Rh(111)	0.715	[7]
Toluene	(4x2)Pt(111)	0.745	[8]
Naphthalene	(3x3)Pt(111)	0.851	[9]
Cyclohexane	$\begin{pmatrix} 4 & -1 \\ 1 & 5 \end{pmatrix}$Pt(111)	1.014	[10]
n-butane	Pt(111)	0.813	[10]
	Ag(111)	0.786	[11]
n-hexane	Pt(111)	0.800	[10]
	Ag(111)	0.843	[11]
n-octane	Pt(111)	0.793	[10]
	Ag(111)	0.809	[11]
Glycine	$\begin{pmatrix} 6 & 2 \\ -2 & 8 \end{pmatrix}$Cu(111) Z = 10	0.749	[12]
	Z = 12	0.899	[12]
	Z = 16	1.198	[12]

TABLE 4

Benzene overlayers on metals: packing coefficients (C_{2D}), packing energies (PE) and dipole-dipole energies (DDE), in kcal/mole, for different surface cells. Also indicated is whether each structure has been observed experimentally. The notation Nx indicates a cell with an area N times the area of the (1x1) metal surface unit cell (N is the determinant of the cell matrix).

Surface	Cell	Type	C_{2D}	PE	DDE	Experimentally found?
Rh(111)	$\begin{pmatrix}3 & 2\\ 1 & 3\end{pmatrix}$[a]	7x	0.790	-4.0	0.42	yes
	$\begin{pmatrix}3 & 1\\ 1 & 3\end{pmatrix}$[b]	8x	0.692	-2.7	0.35	yes
	$\begin{pmatrix}3 & 3\\ -1 & 2\end{pmatrix}$	9x	0.615	-1.9	0.29	no
	$\begin{pmatrix}3 & 0\\ 0 & 3\end{pmatrix}$[c]	9x	0.615	-1.5	0.29	yes
	$\begin{pmatrix}2 & 3\\ -2 & 2\end{pmatrix}$	10x	0.553	-1.6	0.26	no
	$\begin{pmatrix}4 & 3\\ -1 & 2\end{pmatrix}$	11x	0.503	-1.5	0.23	no
	$\begin{pmatrix}1 & -3\\ 3 & 3\end{pmatrix}$	12x	0.462	-0.7	0.19	no
	$\begin{pmatrix}1 & -2\\ 4 & 4\end{pmatrix}$	12x	0.462	-1.4	0.21	no
	$\begin{pmatrix}2 & -2\\ 2 & 4\end{pmatrix}$[d]	12x	0.462	-0.4	0.19	no
	$\begin{pmatrix}3 & 3\\ -2 & 2\end{pmatrix}$[e]	12x	0.462[f]	-0.7	0.19	yes
Ni(100)[g]	$\begin{pmatrix}1 & -3\\ 2 & 2\end{pmatrix}$	8x	0.689	-2.5	0.34	no
	$\begin{pmatrix}2 & -2\\ 2 & 2\end{pmatrix}$[h]	8x	0.689	-2.8	0.35	yes
	$\begin{pmatrix}1 & -3\\ 3 & 0\end{pmatrix}$	9x	0.612	-1.7	0.29	no
	$\begin{pmatrix}3 & 0\\ 0 & 3\end{pmatrix}$[c]	9x	0.612	-1.8	0.29	no

(cont.)

TABLE 4 cont.

Pt(111)[i]	$\begin{pmatrix} 4 & 4 \\ -2 & 2 \end{pmatrix}$[j]	16x	0.646	-2.2	-	yes
	$\begin{pmatrix} 5 & 5 \\ -2 & 2 \end{pmatrix}$[k]	20x	0.516	-0.8	-	yes
Ni(111)	$\begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}$[c]	9x	0.707	-2.6	0.35	no
	$\begin{pmatrix} 1 & -3 \\ 3 & 3 \end{pmatrix}$	12x	0.530	-1.1	0.24	no
	$\begin{pmatrix} 2 & -2 \\ 2 & 4 \end{pmatrix}$[d]	12x	0.530	-0.8	0.23	yes
	$\begin{pmatrix} 2 & -2 \\ 3 & 3 \end{pmatrix}$[e]	12x	0.530	-1.2	0.24	no

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a) Also known as $(\sqrt{7}x\sqrt{7})R19.1°$
b) Also known as $c(2\sqrt{3}x4)$rect
c) Also known as (3x3)
d) Also known as $(2\sqrt{3}x2\sqrt{3})R30°$
e) Also known as $(2\sqrt{3}x3)$rect
f) May contain 2 molecules per cell, yielding $C_{2D} = 0.924$
g) Limits for the cell search were in this case $0.6 < C_{2D} < 0.97$ and maximum 9x.
h) Also known as c(4x4)
i) The same cells as for Rh(111) were found, with only slightly different C_{2D} and energy values. The two additionally listed cells are observed experimentally and presumably contain 2 molecules each, as assumed here.
j) Also known as $(2\sqrt{3}x4)$rect
k) Also known as $(2\sqrt{3}x5)$rect

FIGURE CAPTIONS

Figure 1 A pictorial definition of the molecular cross-section for two-dimensional packing. The molecule is represented by atomic spheres with Van der Waals radii.

Figure 2 Intralayer energies E (kcal/mole) as a function of the two-dimensional packing coefficient, C_{2D}. Open circles: packing energies for benzene on metal surfaces, from Table 4. Triangles: same for the two Pt(111) cells with Z = 2 shown in Table 4. Full circles: naphthalene on Rh and Pt, from previous work (refs. 1a-b). Open squares: dipole-dipole energy for benzene on metal surfaces.

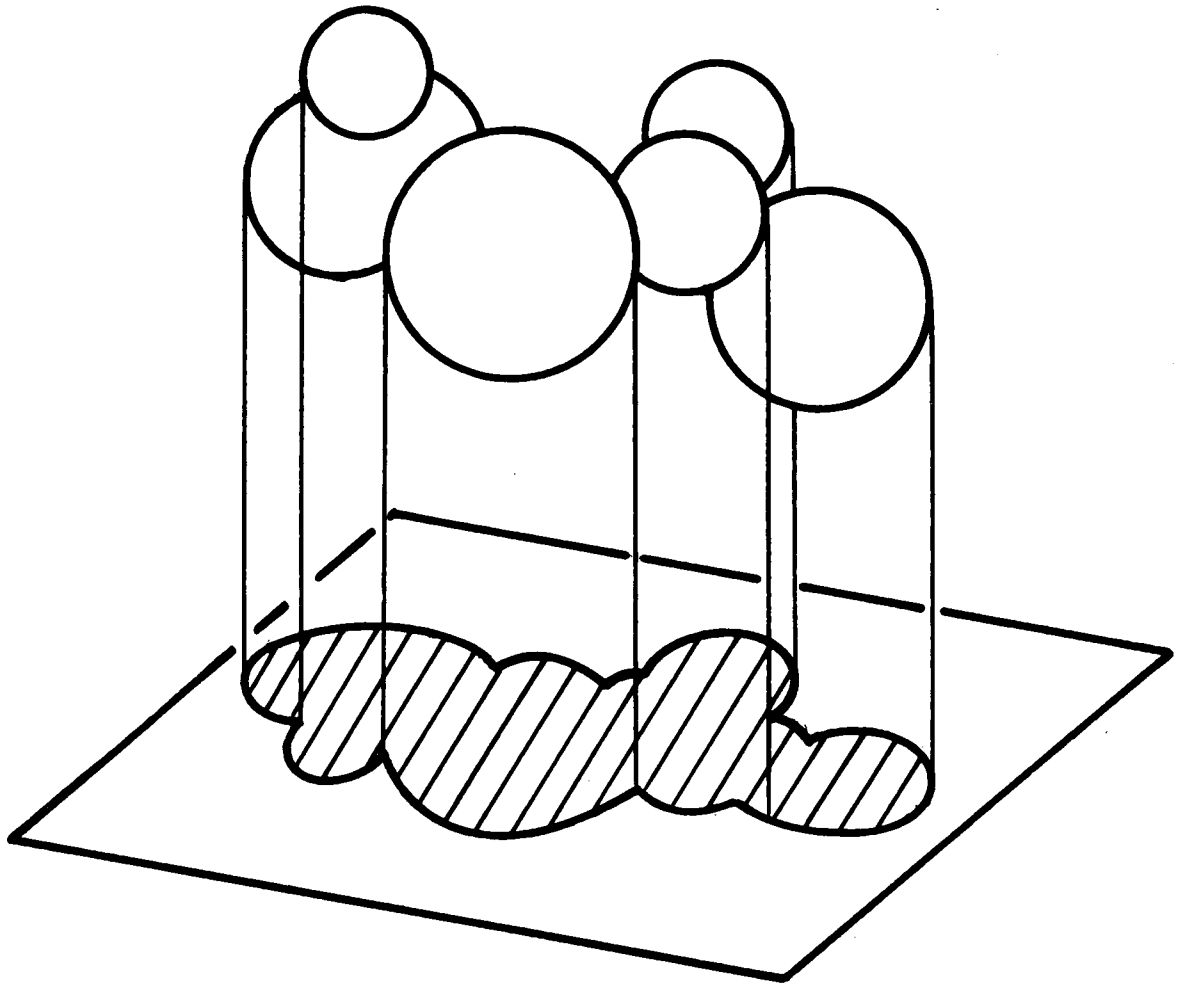

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Figure 1

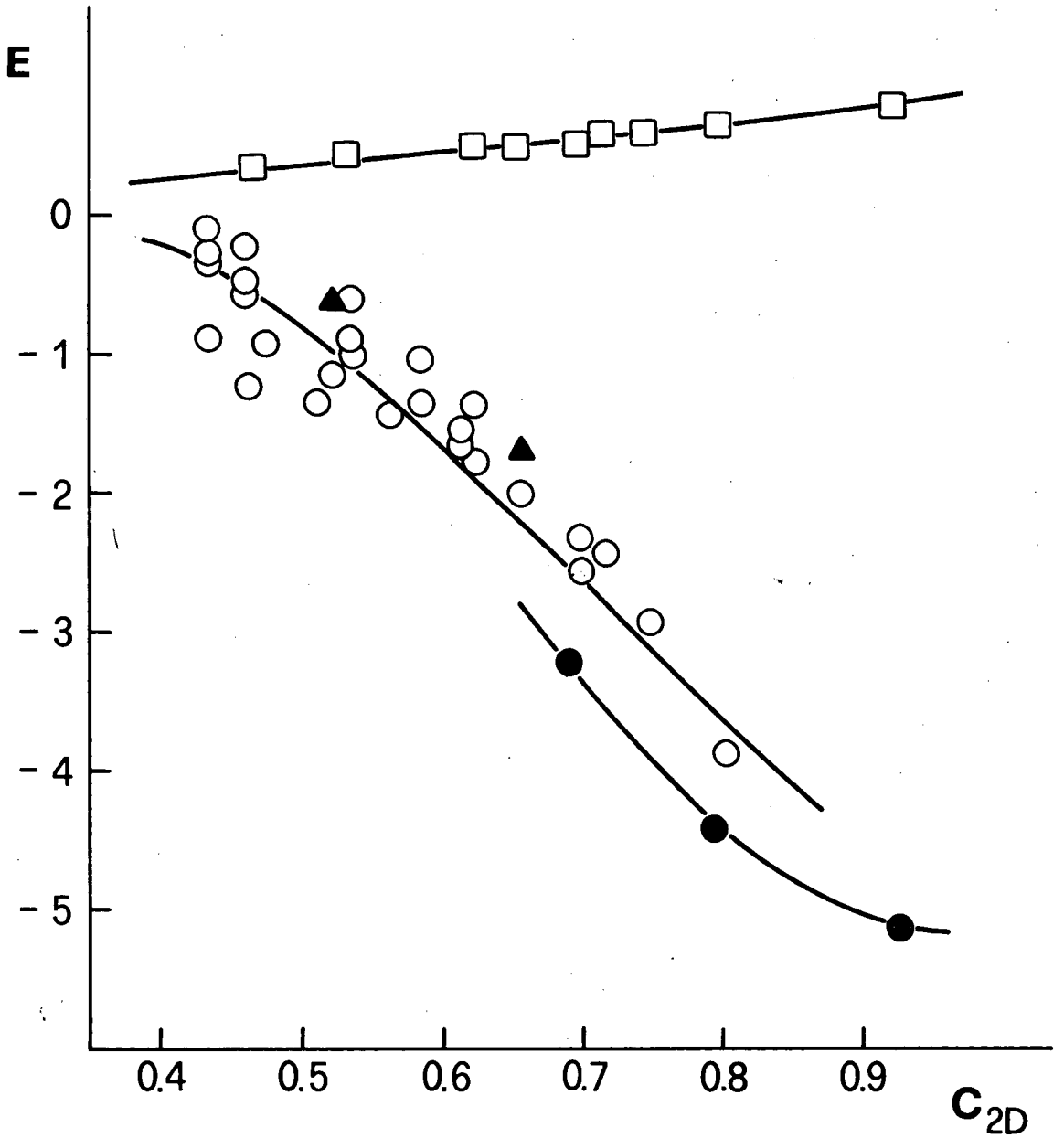

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Figure 2

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