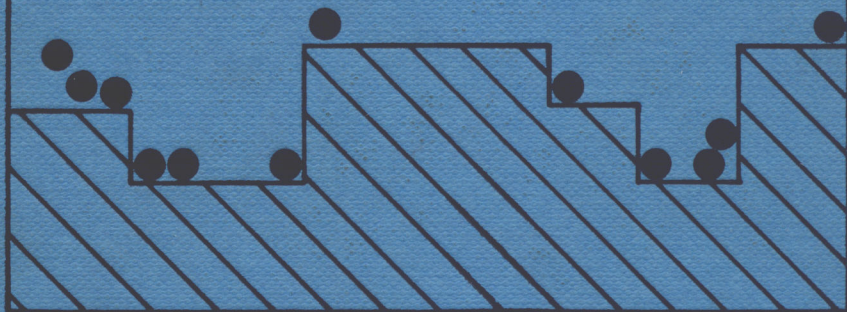# Adsorption of Gases on Heterogeneous Surfaces

By W Rudzinski & D H Everett

Adsorption of Gases on Heterogeneous Surfaces

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Preface

It was Langmuir himself who indicated how his original equation for localised monolayer adsorption on an energetically homogeneous surface could be generalised to describe adsorption on real energetically heterogeneous surfaces. He pointed out that his original equation could be applied to each type of site by the appropriate choice of adsorption parameters, and that the total amount adsorbed could be obtained by averaging these equations using the appropriate weighting factors. This aspect of Langmuir's work was overshadowed by the extensive use of his simple equation, and no attempts were made for many years to investigate the more elaborate forms of the theory.

The first attempts to extend the Langmuir equation eliminated one basic assumption of his theory, namely that the attractive interactions between adsorbed molecules could be ignored, but retained the other assumptions that each molecule occupied one site, and that all sites were characterised by the same adsorption energy. Thus adsorption theory followed the developments of non-electrolyte solution theory in which deviations from ideal behaviour were attributed to intermolecular interactions. The approximations used in these theories, namely the Bragg–Williams and quasi-chemical approximations, were carried over to adsorption theory by Fowler and Guggenheim, and by others.

Meanwhile an alternative approach, again using analogies with bulk systems, pictured the adsorbed gas as a mobile two-dimensional gas exerting a spreading pressure. It was now assumed that deviations of the two-dimensional gas from ideality could be represented by a two-dimensional analogue of the van der Waals equation. This line of thought was developed by Hill and de Boer.

Since an understanding of the basic theory and the effects of intermolecular forces is an essential prerequisite for discussing the influence of heterogeneity, these simpler theories are outlined briefly in Chapter 1.

From an experimental standpoint, many systems were found which did not follow the Langmuir equation, nor some of the other equations developed for homogeneous surfaces. However, it was found possible to describe the

behaviour of such systems in terms of a variety of empirical equations, the theoretical background of which was either unknown or obscure. The more important of these equations are presented in Chapter 2.

Even more dramatic discrepancies between theory and experiment were found in the behaviour of the enthalpies of adsorption and the heat capacities of adsorbed phases, derived either from the temperature dependence of adsorption isotherms, or from direct calorimetric measurements. The presence of attractive interactions between adsorbed molecules should lead to a steady increase in the magnitude of the isosteric enthalpy of adsorption as adsorption proceeds: the majority of systems, however, exhibit the opposite trend. Indeed, the rapid *decrease* in the isosteric enthalpy with increase in the amount adsorbed provided the first compelling evidence for the heterogeneity of real solid surfaces. The behaviour of the heat capacities of adsorbed phases, especially at low temperatures, provided further evidence for heterogeneity. The results of such calorimetric studies are discussed briefly in Chapter 3.

It was not until the end of the 1930s that serious attempts were made to take proper account of the effects of the heterogeneity of solid surfaces on adsorption phenomena. The work was initiated in the USSR by Zhuchovitsky, Roginsky, Todes and Bondareva, but was disrupted by World War II. They introduced both the condensation approximation and the Stieltjes transform methods of treating the problem, but their work, published in an obscure Ukrainian journal, edited in a remote part of the Soviet Union, remained largely unknown for several years, and was not pursued in the USSR after the war.

Meanwhile, in the 1940s the problem of surface heterogeneity was taken up by workers in America, in, for example, the papers of Taylor, Halsey, Sips and Zettlemoyer. From that time on the problem of energetic surface heterogeneity has become one of the important features of research on real adsorption systems. Even so it is surprising that the early work of Hill, in 1949, stressing the importance of the topographical character of the heterogeneity, was neglected for so long. On the contrary, the work of Ross and coworkers, who introduced the concept of a heterogeneous surface as an assembly of uniform (homotattic) patches, enjoyed great popularity, even though for many real surfaces a patchwise distribution is less probable than the random distribution introduced earlier by Hill.

One of the main objectives of much of the earlier work was to examine the possibility of providing a theoretical basis for some of the empirical equations by assuming that the surface heterogeneity could be characterised by a particular mathematical form of the distribution of adsorption energies among adsorption sites. The earlier developments of this approach based on the neglect of interactions between adsorbed molecules are discussed in Chapters 4 and 5.

Attempts to relate the adsorption energy distribution to the physical structure of solid surfaces, and to look for some common features of surface heterogeneity, are the main topics dealt with in Chapter 6. This includes a section on the important and highly topical problem of adsorption by porous solids.

The effects of intermolecular forces at low surface coverage were taken account of in the 1960s and 1970s by the virial description of adsorption at low pressures, again drawing on the analogy with the treatment of the non-ideality of bulk gases. The effects of surface heterogeneity were first incorporated into this formalism by Steele, Halsey, Pierotti and Thomas; and later by Rudzinski and coworkers. Chapter 7 discusses this work.

The extension of the theory to take account of intermolecular forces at higher coverages is discussed in relation to mobile and localised adsorption, respectively, in Chapters 8 and 9, while the influence of heterogeneity on multilayer adsorption is the subject of Chapter 10.

The inverse process of deducing information on the nature of surface heterogeneity, i.e. of retrieving the adsorption energy distribution, from measured adsorption isotherms or isosteric enthalpies, was initiated by Adamson and his coworkers, by Drain and Morrison and by Ross and his group. This aspect of the problem has received intensive study during the past two decades. It is still a very active area of research, and its current status is dealt with in Chapter 11.

A majority of work on the adsorption of gases has retained Langmuir's assumption that each adsorbed molecule occupies one site on the surface. While this may be an adequate simplification for small compact molecules, it is unlikely to be realistic for larger, and often more industrially important, molecules such as the n-alkanes. The problem of multisite adsorption on heterogeneous surfaces is at an early stage of development, and is reviewed in Chapter 12.

Finally, a major recent development is the application of computer simulation methods to study the nature of adsorption on heterogeneous surfaces. Both Monte Carlo and Molecular Dynamics techniques have been applied. Progress in this field is rapid and some of the latest results are presented in Chapter 13.

The topic of the adsorption of gases on heterogeneous surfaces has already been the subject of many hundreds of papers, including several important reviews on more specific aspects. There remains a need, however, for a broad yet detailed survey of the present state of the subject. This is attempted in the present book, in which the published work is presented in a comprehensive, yet critical, fashion. The choice of material and its method of presentation reflects to some extent the views of the authors, but it has been our objective to clarify the underlying concepts and to emphasize the

strengths and weaknesses of the various methods of approach. There are still many unsolved problems, and even some controversies. Where they arise we hope to have presented differing views in proper perspective. Nevertheless it is now becoming widely recognised that all real solid surfaces are heterogeneous to a greater or lesser extent, and that this heterogeneity is a necessary consequence of the thermodynamic and kinetic factors involved in their formation.

The structure of this book reflects our intention to provide a handbook summarising in as coherent a form as possible the main features of the whole subject, but also to follow the historical development. Thus some of the simpler, but fundamental, work is to be found in the earlier chapters, while more recent and advanced approaches appear in the later chapters.

No book can be completely up to date nor give an exhaustive account of every paper that has been published. We hope nevertheless that our presentation, together with the bibliographies attached to each chapter, will provide the reader with access to the most significant work in this important area of surface science.

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List of Symbols

A wide range of symbols and nomenclature has been employed in the literature on the adsorption of gases by solids. To have adopted throughout the symbolism used by the original authors would have led to extensive variations in the symbol used for a given quantity and would have made it difficult to present a straightforward and consistent account of the subject. We have therefore adopted, wherever possible, the recommendations of the International Union of Pure and Applied Chemistry.[1-3] In a few instances, however, to make reference to the original papers easier, we have retained the original notation.

Despite this attempt to rationalise the symbolism, it has still been necessary to associate more than one meaning with each symbol. The list which follows indicates the chapter, section or equation in which each usage is introduced.

References

1. Manual of Symbols and Terminology for Physico-chemical Quantities and Units, Appendix II. Part I: Definitions, terminology and symbols in colloid and surface chemistry. *Pure Appl. Chem.*, **31**, 579–638 (1972).
   Part II: Heterogeneous catalysis. *Pure Applied Chem.*, **46**, 71–90 (1976).
2. Reporting Physisorption data for gas–solid systems. *Pure Appl. Chem.*, **57**, 603–619 (1985).
3. *Quantities, Units and Symbols in Physical Chemistry*, IUPAC, Blackwell, Oxford, 1988.

A_s	surface area (1.2.6)
$A_{s,m}$	area of the mth patch (11.5.7)
A	constant in the Freundlich equation (2.2.1, 4.4.1)
A	constant in equations 3.6.1 and 3.6.2
A	standard affinity of adsorption (6.6.1, 6.6.2)
$A_1(\eta), A_2(\eta)$	functions defined in equation 4.5.48
A_0	defined in equation 5.6.2

A_0, A_1, A_2	coefficients in equation 6.4.4
	coefficients in equation 7.5.2
A_1, A_2	defined in equations 10.2.32 and 10.2.33
A^0	$= K$ ratio of partition functions of gas and adsorbate (11.1.2)
A_{k_i}	coefficients in equation 11.7.7
A_m	coefficients in equation 11.10.7
a	activity
a	parameter in the Jovanovic equation (1.4.104)
a	parameter in the Bradley equation (2.2.5)
a	parameter in equation 10.4.5
a	parameter in equation 12.6.5
a	coefficient in the two-dimensional van der Waals equation (1.4.56)
a'_s	defined in equation 1.4.94
a_f	free surface area (1.3.5, 7.2.24)
$a_{n,i}$	coefficients in the series 7.4.27
a_{lv}	interaction parameter in equation 8.4.41
a_i	defined in equation 9.7.3
$\tilde{a}_i$	defined in equation 9.7.20
$\boldsymbol{a}$	vector defined in equation 11.6.5
$\boldsymbol{a}^T$	transpose of vector $\boldsymbol{a}$ (11.6.5)
a_i	coefficient in the spline function (11.7.41)
a_s	area per atom of carbon in basal plane of graphite
a_{1i}, a_{2i}	coefficients in expansion 11.9.36
a_i	defined in equation 11.11.16
B	constant in the Dubinin–Radushkevich (DR) equation (2.3.2)
B	constant in equation 3.6.2
B	coefficient in the generalised energy distribution (10.3.30)
B_i	coefficient in the generalised DR equation (4.4.9)
B^0	median value of B in the generalised DR equation (6.6.13)
B_0, B_1, B_2, B_3	coefficients in equation 6.4.12
$B_0, B_1, B_2 \ldots$	coefficients in equation 11.2.7
B_l	cluster integrals (7.1.4)
B_1, B_2, B_3	cluster integrals defined in equations 7.1.5–7.1.7
$B_2^{(2D)}$	second two-dimensional virial coefficient (1.4.87)
$B_2^{(2D)*}$	reduced second two-dimensional virial coefficient (1.4.98) $= B_2^{(2D)}/b$

$B_3^{(2D)}$	third two-dimensional virial coefficient (1.4.88)
$B_3^{(2D)*}$	reduced third two-dimensional virial coefficient (1.4.98) $= B_3^{(2D)}/b^2$
$B_4^{(2D)}$	fourth two-dimensional virial coefficient (1.4.98)
$B_4^{(2D)*}$	reduced fourth two-dimensional virial coefficient (1.4.98) $= B_4^{(2D)}/b^3$
$B_{(l+1)s}$	$= l(B_l - B_l^0)$ gas–solid virial coefficients (7.1.15)
B_{2s}, B_{3s}, B_{4s}	gas–solid pseudo-virial coefficients defined in equations 7.1.18–7.1.20
$B_{2s}^{(h)}$	second gas–solid virial coefficient for heterogeneous surface (7.2.6)
$B_{2s}^{(0)}$	second gas–solid virial coefficient for homogeneous surface (7.2.21)
B_n	nth Bernoulli number
b	area occupied by one adsorbed molecule (1.2.25); $= \pi r_0^2/2$, (1.4.51)
b_m	area occupied by one molecule in a filled monolayer (5.6.2)
b	constant in the Tóth equation (2.5.1)
b	constant in the Langmuir equation (5.2.3)
b_i	Langmuir constant for sites of kind i (5.2.1)
b_0	pre-exponential factor in the Langmuir constant (5.2.3)
b	constant in equations 6.4.9 and 6.4.13
b	'shifting factor' or affinity coefficient in equation 6.6.1
b	temperature-dependent parameter in equation 10.4.5
b	$= 2\varepsilon_1/kT$ defined in equation 9.2.3b
b'	temperature-dependent parameter in equation 11.7.20
b'	constant characterising lateral field on graphite (8.4.8)
b_l	lth-order cluster integral in second adsorbed layer (10.4.15)
b_0, b_1, b_2	coefficients in the series 11.2.6
b_i	coefficient in the spline function (11.7.41)
C	parameter in the Temkin equation (2.4.1)
C	normalisation factor in equations 1.4.37, 9.7.32 and 10.2.26
C	correlation function in equation 7.3.27
C_n	normalisation constant in equation 11.2.1
C^α	$= n^a/A_s$ reciprocal of the surface area per unit amount of solid adsorbent (1.2.6)
C^M	$= n^a/M$ reciprocal of the number of adsorption sites per unit amount of solid adsorbent (1.2.7)

C_p^s, C_v	heat capacities of adsorbate defined in equations 1.2.46 and 3.5.8
C^c	heat capacity of calorimeter (1.2.44)
C_γ	defined in equation 1.4.37
$C_{v,xy}, C_{v,z}$	contributions to heat capacity from vibrations in the xy plane and z coordinate (3.5.8)
C_Γ	heat capacity near the critical temperature (3.6.1)
C_Γ^+	heat capacity just above the critical temperature (3.6.9)
C_Γ^-	heat capacity just below the critical temperature (3.6.12)
C_n	coefficients in the expansion 7.4.11
C_{ns}	nth exponential gas–solid virial coefficient (7.5.8)
C^{conv}	heat capacity conversion term (8.6.21)
C_n^r, C_n^p	coefficients in expansion 9.4.13 for random and 9.4.14 for patchwise topography
C_i	$= 1/D_i$ defined in equation 10.4.20
$\hat{C}(Y)$	'average of adsorption strengths' (10.4.23a)
$\bar{C}^n$	defined by equation 10.4.26
C_r	defined by equation 10.4.26
C_1, C_2	coefficients in equation 11.2.5
$C^{(c)}$	normalisation constant in equation 11.7.24
C_n^s	integral defined in equation 11.9.14
C_1^s	constant defined in equation 12.6.9
C_2^s	defined in equation 11.9.15
C_2^p	defined in equation 11.9.16
C_{cor}	defined in equation 11.9.29
C_4^p, C_4^r	defined in equations 11.11.6 and 11.11.7
c_p^g	molar heat capacity of gas at constant pressure (1.2.44)
c_p^s	molar heat capacity of adsorbate at constant pressure (1.2.44)
c	coordination number of lattice, number of nearest neighbours (1.4.2)
c	parameter in the Temkin equation (2.4.1)
c_i	fraction of surface with sites of kind i (5.2.1, 7.2.8)
c_0, c_1	coefficients in expansion 8.4.35
c_0	parameter in the Morse potential (9.5.10)
$c_{ij}(R)$	distribution of site pairs i, j at a separation R
c	parameter in the BET equation (10.3.4, 10.3.53, 10.3.54)
c'	$= c \exp(-\varepsilon/kT)$, equation 10.3.17
c''	$= c' \exp\{r\varepsilon_c - B\varepsilon_0^2\}$, equation 10.3.35
c_i	coefficients in expansion 11.7.17
c_i'	coefficients in expansion 11.7.19

c_i	coefficients in spline function (11.7.41)
c	parameter in the distribution function (12.6.1)
c_n	$= nc$ (12.6.14)
c_v	shear wave velocity in crystal (10.5.1)
D	parameter in the Gottwald–Haul equation (2.6.2)
D_n	nth virial coefficient defined in equation 7.5.10
D	determinant defined in equation 9.1.44
$D_0, D_2 \ldots$	coefficients in equation 9.4.28
D_i	defined in equation 10.4.20
D^n	defined in equation 10.4.26
$D^*(T)$	thickness of film at onset of superfluidity (Section 10.5)
D	diameter of oxygen anion in sphere packing (Section 13.5)
D_{2n}	coefficient defined in equation 11.9.30
d	exponent in equation 4.5.49
d	power of distance in equation 10.2.27
d	coefficient in spline function (11.7.41)
d_1, d_2	defined in equation 11.8.23
d	distance between lattice sites (Section 13.3)
E_u	Euler constant (5.7.4)
E	parameter in equation 6.6.1
E_0	value of E for reference substance (6.6.1)
$E_{n+1}(\theta)$	$(n + 1)$th-order exponential integral
E_t	total energy (8.5.3)
E_k	kinetic energy (8.5.3)
$E_0, E_1, E_2 \ldots$	coefficients in equation 10.4.2
E	defined in equation 10.4.3
$E_i(-ax)$	defined in equation 10.4.8b
e	'two-dimensional internal energy omitting ε' (8.6.16)
e	error vector (11.6.3)
F	Helmholtz (free) energy
F^s	surface Helmholtz energy (1.2.9)
$\hat{F}^s$	$= F^s/A_s$ areal Helmholtz energy (3.6.4)
F_0	contribution to Helmholtz energy from interaction with the surface (3.5.1)
F_u	contribution to Helmholtz energy from adsorbate–adsorbate interactions (3.5.1)
F_v	contributions to Helmholtz energy from vibrations relative to the adsorption site (3.5.1)

$F_{v,xy}, F_{v,z}$	contributions to F_v from vibrations in xy plane and normal to the surface (3.5.2)
F	hypergeometric function defined by equation 5.4.14 or 5.4.17
$F(B)$	differential distribution of B in various types of micropore (6.6.2)
$\langle F \rangle$	average of a physical property F over the surface (7.3.1)
$F_n(s)$	Bose–Einstein integral (8.5.14)
$_1F_1$	defined in equation 10.4.11
F_L	defined in equation 11.7.16
$F(x)$	defined in equation 11.8.10
f_{ij}	$= \exp[-u(r_i, r_j)/kT] - 1$ (1.4.89)
f_{mp}	terms in the Taylor expansion (3.6.6, 3.6.8)
$f(y)$	function defined in equation 4.5.5
f_η	function defined in equation 4.5.36
$\hat{f}_i$	local coverage of sites of the ith kind (5.2.7)
f_r	function of r in equation 6.5.9
f	fraction of surface substituted by foreign atoms (7.2.30)
f_1, f_2	defined in equation 9.2.8
f_i	discrete energy distribution (9.7.1)
$f_{ij}(R)$	correlation function defined in equation 9.7.5
f_v	frequency of oscillation of quartz crystal (10.5.1)
$f(\tau)$	defined in equation 11.7.36
$f(x)$	function defined in equation 11.8.5
f_i	coefficient in expansion 11.8.17
f_i	fraction of adsorption sites with adsorption energy ε_i (9.7.1, 12.2.10)
$f_{i(j)}$	fraction of adsorption sites of type i occupied by segments of type j (12.2.18)
G	Gibbs (free) energy
G^s	surface Gibbs energy (1.2.10)
G	function introduced by Rudnitsky and Alexeyev (5.4.12)
G	function defined in equation 6.7.31
G_1, G_2	one- and two-particle distribution functions defined by equations 7.3.6 and 7.3.7
$G(N_{11})$	number of all possible arrangements for N_{11} (9.1.4)
G_i	fitting parameter in equation 10.2.55
G_L	Laplace transform (11.7.14)
$G(y)$	introduced in equation 11.8.7, defined in equation 11.8.8
$g(w, \theta_1)$	function defined in equation 11.7.25

$g(y)$	function defined in equation 11.8.5
g_j	coefficient in expansion 11.8.16 defined in equation 11.8.18
$g(N_t, M, \{N_{ij}\})$	combinatorial factor in equation 12.3.2
g_0	combinatorial factor for homogeneous surface (12.3.4)
H	enthalpy
$H^s = U^s + pV^s$	surface enthalpy (1.2.8)
H_{ij}	covariant matrix (7.3.20)
$H(\varepsilon)$	function defined by equation 9.4.27
$H, \hat{H}$	Hamiltonian of system (9.7.2, 13.3.3)
H_0	model Hamiltonian (9.7.8)
H_1	interaction Hamiltonian (9.7.8)
H	unit step function at $x = 0$ (10.5.3)
$H_L(p)$	function defined in equation 11.7.21
$H(x, y)$	defined in equation 11.8.9
h	Planck's constant
h	molar enthalpy
h^s	mean molar enthalpy of adsorbate (1.2.28)
h^g	mean molar enthalpy of gas (1.2.28)
$\Delta_a h$	mean molar enthalpy of adsorption (1.2.29)
$-\overline{\Delta_a h}$	$= -$(differential molar enthalpy of adsorption) $=$ (isosteric enthalpy of adsorption) $= q^{st}$ (1.2.38)
h_i	Hamiltonian for internal degrees of freedom (9.7.3)
h_{ij}	integral defined in equation 11.8.15
I_1, I_2, I_3	integrals defined in equations 8.4.21, 8.4.31, 8.4.34
I_1	integral defined in equation 9.6.3
I	integral defined in equation 10.2.28
$I_s(u)$	integral defined in equation 10.3.21
I	identity matrix (11.6.6)
$J(x)$	distribution function of slit sizes (x) (6.6.16)
J_1, J_2, J_3, J_4	integrals in equations 7.3.30, 7.3.32, 7.3.33
J_i	fitting parameter in equation 10.2.55
J_i	Jacobi polynomial (11.8.28)
j	James–Martin compressibility factor (7.5.4)
K	pre-exponential factor in adsorption equilibrium constant in general
K_l	equilibrium constant for localised adsorption (1.4.15)
K_m	equilibrium constant for mobile adsorption (1.4.64)

$K_{m,i}$	equilibrium constant for mobile adsorption on ith patch (8.2.10)
K^L	$= K^{FG}$ adsorption equilibrium function for Langmuir and Fowler–Guggenheim equations (4.3.31)
K^{HB}	adsorption equilibrium function for Hill–de Boer equation (4.3.36)
K^F	Freundlich adsorption constant (6.5.8, 6.6.23)
K^H	Henry's law constant (7.4.8)
K_η^0	constant defined in equation 4.5.31
$\bar{K}_m$	mean value of K_m defined in equation 8.2.12
K_α	force constant in harmonic potential (8.5.17)
$\bar{K}_p$	equilibrium constant in equation 9.6.1
K_T^*	defined in equation 9.7.29
K	$= A^0$ defined in equation 11.1.2
K'	equilibrium constant defined in equation 11.2.4
K'	equilibrium constant defined in equation 12.5.8a
K_I^0	temperature-dependent constant in equation 12.6.3
k	Boltzmann's constant
k_z	force constant for vibration normal to the surface (7.2.19, 9.5.1)
k_z^*	force constant for vibration normal to the surface at the minimum of $U(z)$ (7.2.20)
k'	$= p^0/p^*$ defined in equation 10.3.38
k_i	integers in equation 11.7.6
$k_H(x, y)$	Henry's law constant over point (x, y) on surface (13.5.2)
L	Avogadro's constant
L	molar latent heat of vaporisation (2.3.5)
L	temperature-dependent parameter in equation 5.4.32
$L(\sigma, T)$	lateral size of superfluid domain at coverage σ (Section 10.5)
L	number of terms in the series 11.2.10
L_2	linear space of function (11.8.13)
l_1	integer in equation 11.7.6
M	number of adsorption sites (1.2.6)
M	constant in equation 2.3.5
$M_{ij}(R)$	number of pairs of sites i, j at distance R (9.7.4)
M	matrix in equation 11.6.5
M^*	amount of sites per gram of adsorbent (Tables 12.2, 12.3)

m	mass of adsorptive molecule (1.3.5)
m	constant in Tóth equation (2.5.1)
m	constant in Gottwald–Haul equation (2.6.2)
m	order of critical point (3.6.5)
m_1	parameter in equation 4.5.24
m	molar mass (6.6.32)
m	integer in general adsorption potential equation (7.2.1)
m	running index of patch number (11.5.8)
m_1	integer in equation 11.7.6
N	number of molecules in adsorbed layer (Section 1.4.1)
N_{11}	number of pairs of molecules on adjoining sites (1.4.1)
N_{01}	number of adjoining sites of which one is empty and the other filled (1.4.2)
N_{01}^*	equilibrium value of N_{01} (1.4.38)
N_m	monolayer coverage (Table 5.3) (8.4.43)
N_i, N_0	number of atoms on solid surface with excess energy $u_i^{(ex)}$, u_0 (6.2.1)
N_a	amount adsorbed from solution (6.6.23)
N^g	number of molecules in gas phase (7.1.10)
N^s	number of molecules adsorbed (7.1.10)
N^*	number of molecules adsorbed in second and higher layers (10.3.40)
N_t	total adsorbed amount (11.8.3)
N_{ij}	number of adsorption pairs: sites of type i occupied by segment of type j (12.3.2)
n	amount of substance
n^a	amount of solid adsorbent (Section 1.2)
n^s	amount of adsorbed gas (Section 1.2)
n	parameter in Freundlich equation (2.2.1)
n	parameter in Γ-function (6.6.19)
n	parameter in energy distribution (6.6.29)
n	integer in general adsorption potential equation (7.2.1)
n_f	number of particles on site f: site empty, $n_f = 0$; site full, $n_f = 1$ (Section 9.7) (9.7.2)
n_i	probability that a site i is occupied (9.7.15)
$\tilde{n}$	reduced density $= n(\sigma^{gg})^3$ (Section 10.2)
n_b	bulk density (Section 10.2)
n^l	number of adsorbed layers on surface (11.7.1)
n_i	number of groups (segments) of type i in polymer molecule (12.2.44)