Fundamentals of Interface and Colloid Science

VOLUME IV: PARTICULATE COLLOIDS

J Lyklema

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FUNDAMENTALS OF INTERFACE AND COLLOID SCIENCE

GENERAL PREFACE

Fundamentals of Interface and Colloid Science (FICS) is motivated by three related, but partly conflicting observations.

First, interface and colloid science is an important and fascinating, though often undervalued, branch of science. It has applications and ramifications in domains as disparate as agriculture, mineral dressing, oil recovery, the chemical industry, biotechnology, medical science and many more provinces of the living and non-living world.

The second observation is that proper application and integration of interface and colloid science requires, besides factual knowledge, insight into the many basic laws of physics and chemistry upon which it rests.

In the third place, most textbooks of physics and chemistry pay only limited attention to interface and colloid science.

These observations lead to the dilemma that it is an almost impossible task to simultaneously master specific domains of application and be proficient in interface and colloid science itself, together with its foundations. The problem is aggravated by the fact that the study of interface and colloid science requires a very wide scope of basic underlying sciences; it uses parts of classical, irreversible and statistical thermodynamics, optics, rheology, electrochemistry and other branches of science. Nobody can be expected to command all of these simultaneously.

The prime goal of FICS is to meet these demands systematically by treating the most important interfacial and colloidal phenomena starting from basic principles of physics and chemistry, whereby these principles are first reviewed. In doing so, it will become clear that common roots often underlie seemingly different phenomena, which is helpful in identifying and recognizing them.

Given these objectives, a systematic and deductive approach is indicated. Progressing through the work, systems of increasing complexity are treated, with, as a broad division, in Volume I the fundamentals (F), in Volumes II and III isolated interfaces (I) and in Volumes IV and V interfaces in interaction and colloids (C).

The chosen systematic-deductive set-up serves two purposes: the work is intended to become a standard reference containing parts that will be suitable for systematic study, either as a self-study guide or as a text for courses.

In view of these objectives, a certain style is more or less defined and contains the following characteristics:

- Topics are primarily arranged by the main principle(s) and phenomena on which they rest. As FICS is a book of fundamentals and principles rather than a book of facts, no

attempt is made to give it an encyclopaedic character, although important data are tabulated for easy reference. For factual information, references are made to the literature, in particular to reviews and books. Experimental observations that illustrate or enforce specific principles are emphasized, rather than given for their own sake. No attempt is made to strive for completeness, which also implies a certain preference for illustrations with model systems. Some arbitrariness cannot be avoided; our choice is definitely not a "beauty contest".

- In view of the fact that much space is reserved for the explanation and elaboration of principles, we had to restrict the number of systems treated in order to keep the size of the work manageable. Given the importance of interfacial and colloid science for biology, medicine, pharmacy, agriculture, etc., "wet'" systems, aqueous ones in particular, are emphasized. "Dry" subjects, such as aerosols and solid-state physics, are given less attention.

- Experimental techniques are prone to ageing and are not described in great detail except where they have a typical interfacial or colloidal nature.

- In order to formulate physical principles properly, some mathematics is unavoidable and we cannot always avoid complex and abstract formalisms. To that end, specialized mathematical techniques that are sometimes particularly suitable for solving certain types of problems will be introduced when needed; some of these are in the appendices. The reader is assumed to be familiar with elementary calculus.

- Generally, the starting level of Volume I is such that it can be read without having an advanced command of physics and chemistry. In turn, for the later Volumes, the physical chemistry of Volume I is the starting point.

- To assist the reader in finding his way in this magnum opus, each Volume has an extensive subject index. Moreover, consistency of symbols is strived for.

Considering all these features, FICS may be thought of as a work containing parts that can also be found in more detail elsewhere, but rarely so systematically and in the present context. Moreover, it stands out by integrating all these parts. It is hoped that through this integration many readers will use the work to find their way in the expanding literature and, in doing so, will experience the relevance, beauty and fascination of interface and colloid science.

Hans Lyklema
Wageningen, The Netherlands
2004

PREFACE TO VOLUMES IV AND V: COLLOIDS

After the systematic treatment of Fundamentals (Volume I) and Interfaces (Volumes II and III), FICS is now complete with these two Volumes on Colloids. With respect to style and set-up the present volumes are similar to the previous ones, but with respect to authorship I had the benefit of a large number of (co-) authors.

Continuing along the lines of Volumes II and III, the emphasis is mostly on the basic principles, although in some places the subject matter required a more thematic approach, especially in Volume V. In selecting the themes to be treated we were led by the desired emphasis on fundamentals, implying that complicated multivariable systems had to be shunned, although FICS does help to approach such systems. For instance, recent hot topics like nanocolloids, polymer-surfactant interactions and multilayer polymer adsorption are not treated, but building bricks for these can be found. The fact that the previous Volumes I (1991), II (1995) and III (2000) continue to sell regularly in successive prints proves the point that fundamentals do not age, although colloid science continues to rejuvenate itself.

The level of Volumes IV and V is comparable with that of Volumes II and III, to which reference is often made. As compared with these Volumes, the presentation of the various chapters shows more variety. This is partly caused by the differences between the aims of these chapters and partly by the multi-authorship. We can live with some variety, provided the typical style elements are maintained. To group the topics into two manageable parts, the somewhat arbitrary division between "particulate", or "hard" colloids (Volume IV) and "soft" colloids (Volume V) was made. Besides this, Volume IV emphasizes general principles, whereas Volume V is rather thematic.

Volumes IV and V are written in such a way that they can be read without having the other Volumes at hand. To that end, basic equations and notions are repeated where appropriate. For further details, extensive references are made to previous volumes. In doing that, we strived for consistency with respect to symbols and nomenclature.

Technicalities. In a book with a scope as wide as FICS, clashes must be expected regarding symbols and units of quantities. This is even more of a problem with the present Volumes, where the authors come from fields as disparate as chemical physics, technology, macromolecular science and "just" physical and colloid science. Each of these fields cherishes its own symbols and habits. As FICS does not primarily address these fields, but wants to present an integrated overview, uniformity of symbols is a must. Since the appearance of Volume I we heeded IUPAC recommendations, being the most appropriate international endeavour of harmonizing this issue. A list of symbols is added.

General deviations from IUPAC rules include our using F for Helmholtz energy, instead of A, because of the obvious confusion with A for area. In some cases clashes had to be dealt with, either by accepting a local deviation (with local explanation), for instance for G (Gibbs energy) and G (modulus) occurring in the same equation (chapter IV.6) or with Π for osmotic and disjoining pressure (chapter V.1), with the same problem.

Regarding the spelling of names, we prefer that of the country of origin. So, with respect to people we refer to d'Arcy, van der Waals and Deryagin, instead of Darcy, VanderWaals and Derjaguin. For phenomena and laws, capitals are used (Van der Waals equation), so consistency may require having van der Waals and Van der Waals in one and the same sentence. References to the literature must always be verbatim; it is unavoidable that this introduces additional spelling variations.

Regarding the transcription of Slavic names, that of the *Chemical Abstracts* is heeded, except where the publishers or the authors themselves used a different transcription. As there is no generally accepted alternative to the C.A. rules, this gives rise to some disparities that are mostly not serious. For instance, one may find Rehbinder next to Rebinder and Slyezov or Slyozov next to Slezov.

Dr. G. Nägele for making available the theoretical and computer simulations data of fig. 5.31a and b, Prof. H.N.W. Lekkerkerker for useful discussions, Dr. P. Royall for the data for fig. IV.5.4 and Mrs. I. van Rooijen and Mr. J. den Boesterd for help with the preparation of figures. Prof. Ericsson acknowledges the fine cooperation with Dr. Stig Ljunggren, of which he has greatly benefited.

As with the previous Volumes, the layout, typing and masterminding computer and printing problems was in the skillful and competent hands of Josie Zeevat-van Homelen, who even under adverse conditions continued to be inspiring and enthousiastic. FICS is not only my book, but also hers. The artwork was again in the capable hands of Mr. G. Buurman. He was able to secure homogeneity across figures supplied from various origins. Mrs. de Keizer assisted me with literature retrieval. Several people in the department helped with odd jobs; among them I specially mention Mr. A.W. Bouman.

Outside our department Mrs. M. Tuinier-Kröner and Mrs. L. de Jong have been very helpful with structuring and converting texts into FICS style and/or setting up early texts.

Last but not least, I express my sincere gratitude to my wife for her continuing understanding and tolerance.

Many stories never end. Let us hope that this is also the case with interface and colloid science. In this vein, I would like to dedicate these books to all those who continue to be fascinated with this realm of science, searching for the roots behind phenomena. More personally I dedicate FICS to my inspirator, Prof. J.Th.G. Overbeek, who taught me how to think and how to implement insights.

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LIST OF FREQUENTLY USED SYMBOLS (Volumes I-V)

Symbols representing physical quantities are printed in *italics*.
Thermodynamic functions: capital for macroscopic quantities, small for molecul-
ar or subsystem quantities (example: U = total energy, u = pair energy between
molecules).

Superscripts

†	standard pressure
o	standard in general
*	pure substance; complex conjugate
σ	interfacial (excess)
(σ)	interaction at constant charge
(ψ)	interaction at constant potential
E	excess, X (real) – X (ideal)
S, L, G	in solid, liquid or gaseous state
⊥	normal to surface
//	parallel to surface

Subscripts

m	molar (sometimes molecular)
a	areal (per unit area)
g	per unit mass

Recurrent special symbols

$O(10^{20})$	of the order of 10^{20}
ΔX	X (final) – X (initial). Subscript attached to Δ to denote type of process: ads (adsorption, diss (dissociation), hydr (hydration), mix (mixing), r (reaction), sol (dissolution), solv (solvation), subl (sublimation), trs (transfer), vap (vaporization, evaporation), etc.

Some mathematical signs and operators

Vectors	**bold face.** Example: F for force, but F_z for z-component of force
Tensors	**bold face** with tilde ($\tilde{\tau}$)

complex quantities bear a circumflex ($\hat{n}$), the corresponding conjugate is $\hat{n}$ *

$\|x\|$	absolute value of x
$\langle x \rangle$	averaged value of x
$\bar{x}$	Fourier or Laplace transform of x (sometimes this bar is omitted)

For vectorial signs and operators (∇, ∇^2, grad, rot, and $\times$), see I.appendix **7**.

Latin

a		activity (mol m^{-3})
	$a_{\pm}$	mean activity of an electrolyte (mol m^{-3})
a		attraction parameter in Van der Waals equation of state (N m^4)
	a^{σ}	two-dimensional attraction parameter in two-dimensional Van der Waals equation of state (N m^3)
a		radius (m)
	a_g	radius of gyration (m)
	a_m	area per molecule (m^2)
A		area (m^2)
	A_g	specific area (m^2 kg^{-1})
A		Hamaker constant (J)
	$A_{ij(k)}$	Hamaker constant for interaction of materials i and j across material k (J)
b		volume correction parameter in Van der Waals equation of state (m^3)
$\mathbf{B}$, B		magnetic induction (T = V m^{-2} s)
$B_2(T)$		second virial coefficient (m^3 mol^{-1} or m^3 molecule^{-1})
	$B_2^{\sigma}(T)$	interfacial second virial coefficient (m^2 mol^{-1}, m^2 molecule^{-1} or –)
c		velocity of electromagnetic radiation in a vacuum (m s^{-1})
c		concentration (usually mol m^{-3}, sometimes kg m^{-3})
c_1, c_2		principal curvatures (m^{-1})
C		(differential) electric capacitance (C V^{-1} or, if per unit area, C m^{-2} V^{-1})
	C^d	(differential) electric capacitance of diffuse double layer (C m^{-2} V^{-1})
	C^i	(differential) electric capacitance of Stern layer (C m^{-2} V^{-1})
C		BET-transformed (-)
C_1		first bending moment (N)
C_2		second bending moment (J)
C_x		(time-) correlation function of x (dim. x^2)
C_p		molar heat capacity at constant pressure (J K^{-1} mol^{-1})
C_V		molar heat capacity at constant volume (J K^{-1} mol^{-1})
C_A^{σ}		interfacial excess molar heat capacity at constant area per unit area (J K^{-1} m^{-2} mol^{-1})
C_{γ}^{σ}		interfacial excess molar heat capacity at constant interfacial tension per unit area (J K^{-1} m^{-2} mol^{-1})
Ca		capillary number (-)
d_f		fractal dimension (-)
d		layer thickness (m)
	d^{ek}	electrokinetic thickness (m)
	d^h	hydrodynamic thickness (m)
	d^{ell}	ellipsometric thickness (m)

	d^{st}	steric thickness (polymeric adsorbates) (m)
D		diffusion coefficient ($m^2\ s^{-1}$)
	D^{σ}	surface diffusion coefficient ($m^2\ s^{-1}$)
	D_r	rotational diffusion coefficient (s^{-1})
	D_s	self-diffusion coefficient ($m^2\ s^{-1}$)
$\mathbf{D},\ D$		dielectric displacement ($C\ m^{-2}$)
De		Deborah number (-)
Du		Dukhin number (-)
e		elementary charge (C)
$\mathbf{E},\ E$		electric field strength ($V\ m^{-1}$)
E		Young's modulus ($N\ m^{-2}$)
E_i		irradiance ($J\ m^{-2}\ s^{-1} = W\ m^{-2}$)
$\mathbf{E}_{sed}$		sedimentation potential ($V\ m^{-1}$)
E_{str}		streaming potential ($V\ m^2\ N^{-1}$)
f		friction coefficient ($kg\ s^{-1}$)
f		activity coefficient (mol fraction scale) (-)
f		fraction of free counterions (-)
f_{ij}		Mayer function for interaction between particles i and j (-)
F		Faraday constant ($C\ mol^{-1}$)
F		Helmholtz energy (J)
	$F_i,\ F_{mi}$	partial molar Helmholtz energy ($J\ mol^{-1}$)
	F_m	molar Helmholtz energy ($J\ mol^{-1}$)
	F^{σ}	interfacial (excess) Helmholtz energy (J)
	$F_a^{\sigma},\ F^{\sigma}/A$	interfacial (excess) Helmholtz energy per unit area ($J\ m^{-2}$)
$\mathbf{F},\ F$		force (N)
$g(r)$		radial distribution function (-)
$g^{(h)}$		hth order distribution function (-)
$g(\mathbf{q},t)$		time correlation function, if real (light scattering usage) (dimensions as C_x)
g		standard acceleration of free fall ($m\ s^{-2}$)
G		Gibbs energy (J)
	G_{xy}	one of the nine components of the bulk modulus ($N\ m^{-2}$)
	$G_i,\ G_{mi}$	partial molar Gibbs energy ($J\ mol^{-1}$)
	G_m	molar Gibbs energy ($J\ mol^{-1}$)
	G^{σ}	interfacial (excess) Gibbs energy (J)
	$G_a^{\sigma},\ G^{\sigma}/A$	interfacial (excess) Gibbs energy per unit area ($J\ m^{-2}$)
$G(z)$		segment weighting factor in polymer adsorption theory (-)
$G(z,s)$		endpoint distribution in a segment of s segments (polymer adsorption) (-)
h		Planck's constant (J s)
$\hbar$		$h/2\pi$ (J s)
h		(shortest) distance between colloidal particles or macrobodies (m) (half distance in ch. V.1)

h, H		height (m)
h		film thickness (m)
	h_{cr}	critical film thickness for rupture (m)
$h(r)$		total correlation function (-)
H		enthalpy (J)
	H_i, H_{mi}	partial molar enthalpy (J mol^{-1})
	H_m	molar enthalpy (J mol^{-1})
	H^σ	interfacial (excess) enthalpy (J)
	H_a^σ, H^σ / A	interfacial (excess) enthalpy per unit area (J m^{-2})
$\mathbf{H}$, H		magnetic field strength (C m^{-1} s^{-1})
$H(p,q)$		Hamiltonian (J)
i		intensity of radiation (V^2 m^{-2})
	i_i	incident intensity (V^2 m^{-2})
	i_o	intensity in a vacuum (V^2 m^{-2})
	i_s	scattered intensity (V^2 m^{-2})
$\mathbf{i}$		unit vector in x-direction (-) (not in chapter I.7)
I_{str}		streaming current (C m^2 N^{-1} s^{-1})
I		ionic strength (mol m^{-3})
I		radiant intensity (J s^{-1} sr^{-1} = W sr^{-1})
$I_x(\omega)$		spectral density of x (dim. x^2 s)
$\mathbf{j}$		unit vector in y-direction (-) (not in chapter I.7)
$\mathbf{j}$, j		(electric) current density (A m^{-2} = C m^{-2} s^{-1})
	$\mathbf{j}^\sigma$, j^σ	surface current density (C m^{-1} s^{-1})
J		compliance (m^2 N^{-1})
$\mathbf{J}$, J		flux (mol m^{-2} s^{-1} or kg m^{-2} s^{-1})
	$\mathbf{J}^\sigma$	surface flux (mol m^{-1} s^{-1} or kg m^{-1} s^{-1})
	J^σ	interfacial compliance (mN^{-1})
J		first, or mean, curvature (m^{-1})
k		Boltzmann's constant (J K^{-1})
k		rate constant (dimensions depend on order of process)
k_1		bending modulus (J)
k_2		saddle splay modulus (J)
$\mathbf{k}$		unit vector in y-direction (-) (not in chapter I.7)
$\mathbf{k}$		wave vector (m^{-1})
$\mathcal{K}$		optical constant (m^2 kg^{-2} or m^2 mol^{-2})
$K(R)$		optical constant (V^4 C^{-2} m^{-6})
$K(\omega)$		absorption index (-)
K		chemical equilibrium constant (general)
	K_p	on pressure basis (-)
	K_c	on concentration basis (-)
K		second, or Gauss, curvature (m^{-2})
K		(integral) electric capacitance (C V^{-1} or C m^{-2} V^{-1})
	K^d	(integral) electric capacitance of diffuse layer (C m^{-2} V^{-1})

	K^i	(integral) electric capacitance of Stern layer ($C\ m^{-2}\ V^{-1}$)
K_H		Henry constant (m)
	k_H	Huggins constant (various dimensions)
K_i		distribution (partition) coefficient (-)
K_L		Langmuir constant ($m^3\ mol^{-1}$)
K		compression modulus ($N\ m^{-2}$)
K		conductivity ($S\ m^{-1} = C\ V^{-1}\ m^{-1}\ s^{-1}$)
	K^σ	surface conductivity ($S = C\ V^{-1}\ s^{-1}$)
	K^σ	interfacial dilational modulus ($N\ m^{-1}$)
L		contour length (polymers) (m)
L_{ik}		cross coefficients in irreversible thermodynamics (varying dimensions)
ℓ_B		Bjerrum length (on surfaces) $= 2r_B$ (m)
ℓ		bond length in a polymer chain (m)
m		mass (kg)
M		(relative) molecular mass (-)
	$\langle M\rangle_w,\ M_w$	ibid., mass average (-)
	$\langle M\rangle_z,\ M_z$	ibid., Z-average (-)
	$\langle M\rangle_n,\ M_n$	ibid., number average (-)
Ma		Marangoni number (-)
n		refractive index (-)
n		number of moles (-)
	n^σ	(excess) number of moles in interface (-)
$\boldsymbol{n}_{x,y,z}$		unit vector in x-, y- or z-direction (-) (chapter I.7 only)
N		number of segments in a polymer chain
N		number of molecules (-)
	N_{Av}	Avogadro constant (mol^{-1})
	N_s	number of sites (-)
p		bound fraction (of polymers) (-)
p		pressure ($N\ m^{-2}$)
	Δp	capillary pressure ($N\ m^{-2}$)
p		stiffness (persistence) parameter (polymers) (-)
$\boldsymbol{p},p$		dipole moment (C m)
	$\boldsymbol{p}_{ind},p_{ind}$	induced dipole moment (C m)
$\boldsymbol{p},p$		($= m\,v$) momentum ($J\ m^{-1}\ s$)
P		probability (-)
$P(q)$		form factor (-)
$\boldsymbol{P},P$		polarization ($C\ m^{-2}$)
Pe		Péclet number (-)
	Pe_t	translational (-)
	Pe_r	rotational (-)
q		heat exchanged (incl. sign) (J)
	$q(\text{isost})$	isosteric heat of adsorption (J)

q		generalized parameter indicating place coordinates in Hamiltonian
q		subsystem canonical partition function (-)
q		electric charge (on ions) (C)
q		persistence length (polymers) (m)
$\boldsymbol{q}$, q		scattering vector (m^{-1})
Q		electric charge (on colloids, macrobodies) (C)
$Q(N,V,T)$		canonical partition function (-)
$Q_{eo,E}$		electro-osmotic volume flow per unit field strength (m^4 V^{-1} s^{-1})
$Q_{eo,I}$		electro-osmotic volume flow per unit current (m^3 C^{-1})
$\boldsymbol{r}$, r		distance (m)
	r_B	Bjerrum length (in bulk) (m)
r		number of segments in a polymer (-)
R		gas constant (J K^{-1} mol^{-1})
R		(principal) radius of curvature (m)
$\boldsymbol{R}$		Poynting vector (W m^{-2})
R_θ		Rayleigh ratio (m^{-1})
Re		Reynolds number (-)
s		sedimentation coefficient (s)
	s_x	relative standard deviation of x (-)
	s	supersaturation ratio (-)
S		entropy (J K^{-1})
	S_i, S_{mi}	partial molar entropy (J K^{-1} mol^{-1})
	S_m	molar entropy (J K^{-1} mol^{-1})
	S^σ	interfacial (excess) entropy (J K^{-1})
	S_a^σ, S^σ / A	interfacial (excess) entropy per unit area (J K^{-1} m^{-2})
$S(\boldsymbol{q},R,\Omega)$		spectral density as a function of $\omega_s - \omega_i = \Omega$ (V^2 m^{-2} s)
$S(\boldsymbol{q},c)$, $S(q)$		structure factor (-)
$S(s)$		ordering parameter of s (-)
t		time (s)
t		transport (or transference) number (-)
T		temperature (K)
Ta		Taylor number (-)
Tr		Trouton number (-)
u		(internal) energy per subsystem (J)
u		(electric) mobility (m^2 V^{-1} s^{-1})
U		(internal) energy, general (J)
	U_i, U_{mi}	partial molar energy (J mol^{-1})
	U_m	molar energy (J mol^{-1})
	U^σ	interfacial (excess) energy (J)
	U_a^σ, U^σ / A	interfacial (excess) energy per unit area (J m^{-2})
υ		excluded volume parameter (polymers) ($= 1-2\chi$)
$\boldsymbol{\upsilon}$, υ		velocity (m s^{-1})