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Álvaro González García

Polymer-Mediated Phase Stability of Colloids

Doctoral Thesis accepted by
Utrecht University, Utrecht, The Netherlands

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Supervisor's Foreword

This year it is exactly 65 years ago that Sho Asakura and Fumio Oosawa in Nagoya, Japan, showed that adding nonadsorbing macromolecules to a colloidal dispersion induced effective attractions between the colloidal particles. In these 65 years, this so-called depletion interaction has proven to be of great significance for colloidal phase stability.

The Ph.D. thesis of Álvaro González García describes the work he performed the past few years at Utrecht University and Eindhoven University of Technology, the Netherlands, which can partly be seen as an extension of the insights of the depletion interaction and resulting phase stability.

Álvaro graduated from his M.Sc. study with honours at Utrecht University, always focused on theory and simulation work of soft matter, with an internship at DSM where he also performed experiments. He demonstrated his ability to quick thinking and learning, by rapidly digging into and mastering the necessary thermodynamics of colloids to be able to do computations and, from the beginning, started to add his own ideas to the problems we worked on. His contributions to the field include the influence of direct interactions (beyond hardcore) between colloids in colloid–polymer mixtures, accurate estimations of free volume available in dense suspensions, the transition between polymer depletion and adsorption in colloid–polymer mixtures, polymer-mediated interactions between block copolymer micelles, and last but not least, extended insights into the phase behaviour of disc–polymer and superball–polymer mixtures. It was clear during the project that Álvaro had a keen interest in anisotropic particles. For that reason, he started to work on mixtures of platelets plus depletants (Chap. 6). At some point, he entered my office with the question: is it possible to have four-phase coexistence in platelet–polymer mixtures? This question made me think. That unique moment that one finds something unexpected...

Several topics he worked on are topics I worked on and thought about for maybe a decade or so (Chaps. 2–5, 8), but which were solved by him to a, in my opinion, satisfactory degree. Very rapidly within the Ph.D. project of Álvaro our working relationship was developing from supervisor–student towards a collaborator role.

He was always up for any new challenge I gave him but also started to have more own ideas.

I am grateful and pleased Springer is publishing this exceptional thesis of Álvaro González García and thank Eindhoven University of Technology and Utrecht University for encouraging interactions between our universities, which stimulated this work.

Eindhoven, The Netherlands
July 2019

Prof. Remco Tuinier

Preface

*I said to the almond tree, "Sister, speak to me of God".
And the almond tree blossomed.*
Nikos Kazantzakis

One may pretend to understand the complex processes that ultimately give the almond tree flower its functional aesthetic characteristics. Such an act of vanity reflects the opposite of the scientific method. In order to grasp the real world, one must simplify it. An effective approach is to select a small number of relevant parameters, and test how robust the predictions extracted from the experimental, computational or theoretical method followed are compared with real-life observations. Note that even experimental laboratory research provides a simplified picture of real systems.

In this thesis, we have isolated some key parameters governing the (in)stability of colloid–polymer mixtures. The term ‘colloid’ refers to a state of matter in which a certain amount of material (with one of its dimensions between one nanometre to one micrometre) is dispersed in another medium. Polymers are macromolecules constituted of many repeating units called segments; depending on the number and nature of these segments, polymers may dissolve or phase-separate in solution. Colloid–polymer mixtures are widespread in biological systems (including blood, the cytoplasm of a living cell, and plant sap), as well as in man-made products (such as paints, drinking yogurt, and printing inks). Better control over the stability limits during product development is possible via a fundamental understanding of the effect of some relevant parameters in the system at hand. In the examples given above, multiple colloids, polymers, and other components are often present. Building knowledge on the interactions between components of the same nature, and pairs of different components is a logical starting point. Based on the characteristics of the colloidal particles investigated, we sequester this thesis into three parts.

In Part I, we took the simplest model system: mixtures of hard *spheres* (like billiard balls) with added polymers simplified as ghost-like spheres. We studied how a direct soft interaction beyond the hardcore interaction modulates the phase stability of a model colloid–polymer mixture (Chap. 2). We conclude that soft repulsive interactions widen the stable region and direct soft attractions decrease the

stability of a colloid–polymer mixture. We also paid attention to mixtures of such colloidal hard spheres with added tiny polymers (Chap. 3): such a model system may be of relevance, for instance, in protein crystallisation. Upon revisiting a well-established (relatively simple) free volume theory, we improved it for the solid phase state, which brought it closer to more convoluted ones, simulations, and experiments. In Chaps. 2 and 3, we (over)simplified the polymers (we took them as a ghost-like sphere), while in Chap. 4 we describe them in more detail. In that chapter, we extract how the strength of the interaction between the surface of the colloidal particle and the polymer segments affects the phase behaviour of a colloid–polymer mixture. We elucidate the possibility of colloid–polymer mixtures which do not phase-separate, even at high polymer concentrations, which is appealing for industrial applications such as paint or foodstuff.

In Part II, we focus on the influence of the shape of the colloidal particle on the phase behaviour of colloid–polymer mixtures. Liquid crystalline phases in non-dilute colloidal dispersions may emerge as a consequence of *the anisotropic shape of particles*. Not surprisingly, the pigment’s shape affects the final properties of paints and coatings. We consider anisotropic hard particles, and study the effects of adding ghost-like spheres to mimic polymer chains. Investigations of cube-like (Chap. 5) and platelet-like (Chap. 6) colloids reveal a rather rich phase behaviour. We highlight the unexpected presence of up to four phases in coexistence in effective two-component systems, reported for the first time in this thesis. Furthermore, we elucidate the relevance of compartmentalisation of tiny compounds in highly concentrated systems. This could be of interest, for instance, in the future development of photonic materials with two different optical paths, and may serve as a model to study crowded living environments.

Finally, in Part III, we studied *association colloids*. We focus on associative colloidal particles formed by diblock copolymers: polymers composed of well-soluble segments and of poorly soluble segments divided into two blocks. In a selective solvent, diblock copolymers can constitute the building blocks of equilibrium structures known as micelles. We focus on self-organised spherical micelles, used in applications ranging from cosmetics to targeted drug delivery to, for instance, tumoral cells. We studied micelle–micelle interactions, and particularly focus on how the building block composition affects colloidal stability (Chap. 7) and how it is affected by the addition of a second (non-blocky) polymer (Chap. 8). The associative and soft nature of association colloids render the problem at hand complex, yet insights could be extracted about the phase stability of micelles. We concluded that spherical micelles resulting from diblocks with a short soluble block are more suitable for applications than those with a large soluble block.

By virtue of these simplified models, a collection of predictions governing the (in)stability of colloid–polymer mixtures has been extracted. These may serve for further developments, considering, for instance, not only two but multi-component mixtures. Further tuning of the accuracy of the models could bring them closer to reality. The author hopes that the small pieces that this thesis has added to the puzzle of knowledge may inspire and be of utility to others.¹

Utrecht, The Netherlands

Álvaro González García

¹Note: The first and last parts of this Summary are (heavily) influenced by the author's article in Cultural Resuena, 'Nikos Kazantzakis y el espíritu científico' (only in Spanish): <http://www.culturalresuena.es/2016/10/kazantzakis-espiritu-cientifico/>

Publications related to this thesis

This thesis is based upon the following publications:

- **Á. González García**, and R. Tuinier. Tuning the phase diagram of colloid–polymer mixtures via Yukawa interactions, *Phys. Rev. E*, **94**, 06260 (Chap. 2)
- **Á. González García**, J. Opdam, R. Tuinier, and M. Vis. Isostructural solid–solid coexistence of colloid–polymer mixtures, *Chem. Phys. Lett.*, **709**, 16–20 (Chap. 3)
- **Á. González García***, J. Nagelkerke*, R. Tuinier*, and M. Vis*. Unipletion in colloid–polymer mixtures, *in preparation* (Chap. 4)
- **Á. González García**, J. Opdam, and R. Tuinier. Phase behaviour of colloidal superballs mixed with non-adsorbing polymers, *Eur. Phys. J. E*; 41:110, 2018 (Chap. 5)
- **Á. González García**, H. H. Wensink, H. N. W. Lekkerkerker, and R. Tuinier. Entropic patchiness drives multi-phase coexistence in discotic colloid-depletant mixtures, *Sci. Rep.*, **7**, 17058, 2017 (Chap. 6)
- **Á. González García**, R. Tuinier, J. V. Maring, J. Opdam, H. H. Wensink, and H. N. W. Lekkerkerker. Depletion-driven four-phase coexistences in discotic systems, *Mol. Phys.*, **116**:21–22, 2757–2572, 2018 (Chap. 6)
- **Á. González García**, R. Tuinier, and A. Cuetos. Compartmentalisation in crowded discotics: quantifying what goes where, *in preparation* (Chap. 6)
- **Á. González García***, A. Ianiro*, and R. Tuinier. On the Colloidal Stability of Spherical Copolymeric Micelles, *ACS Omega* **3** (12), 17976–17985, 2018 (Chap. 7)
- **Á. González García***, A. Ianiro*, R. Beljon, Frans A. M. Leermakers, and R. Tuinier. Polymer-mediated stability of micellar suspensions, *in preparation* (Chap. 8)

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Symbols and Acronyms

Symbols²

$\beta \equiv 1/k_{\text{B}}T$	The inverse of the thermal unit of energy $k_{\text{B}}T$, with k_{B} Boltzmann's constant and T the absolute temperature
r	Centre-to-centre distance between colloids
σ	Colloidal diameter ($\sigma \equiv 2R$, with R the colloidal radius)
W	Interaction potential
q_{Y}	Range of the HCY interaction
ϵ	Strength (contact potential) of the HCY interaction
$\hat{\kappa}$	Screening length of the HCY interaction
$\phi_{\text{d}}^{\text{R}}$	Polymer bulk volume fraction
q	Relative size of polymer to colloidal particle
δ	Adsorption (and depletion) thickness
ζ	Strength of the penetrable sphere (PS) interaction
B_2	Second osmotic virial coefficient
v_{c}	Colloidal particle volume
$B_2^* \equiv B_2/v_{\text{c}}$	Normalised second virial coefficient
F	Helmholtz (free) energy
V	System volume
Λ_{B}	De Broglie thermal wavelength
ϕ_{c}	Colloid volume fraction
$\phi_{\text{c}}^{\text{CP}}$	Colloid volume fraction at close packing
N_{c}	Number of colloids
$\gamma_{\text{Y}}, \gamma_1, \gamma_2, Q_{\text{Y}}, L_{\text{Y}}$	Set of equations defining the free energy following the FMSA
μ_i	Chemical potential of component i
Π	Osmotic pressure
Ω	(semi) grand-potential
α	Free volume fraction for depletants in the FVT framework

²Many symbols used in Sects. 3.2, Appendices 6.1 and 6.2 are intentionally left out of this list.

ϕ_d^S	Depletant volume fraction in the colloid-polymer mixture
v_d	Volume of a depletant
ω	Work
$\langle V_{\text{free}} \rangle_o$	Undistorted free volume for depletants in colloidal system
v_{exc}	Excluded volume
Q_s	Shape-dependent term in FVT upon applying SPT to the probability of inserting a depletant
$y \equiv \phi_c / (1 - \phi_c)$	An auxiliary function commonly used in FVT derivations
N_d^R	Number of depletants in R considered in FVT
λ	Scaling factor of the SPT approach used to calculate α
κ	Total number of depletion zones overlaps within a UC
ϕ_c^*	ϕ_c from which depletion zones overlap for HSs in a FCC lattice
o	Undistorted properties (depletant-free system, isolated micelle)
ϕ_k	Volume fraction of components in the SCF-lattice, such that: ϕ_A , solvophilic block; ϕ_B , solvophilic block; ϕ_p , micelle forming polymer; ϕ_G , added guest homopolymer to the colloidal suspension; and ϕ_W , solvent (never graphically presented).
N_{lat}	Number of lattice sites considered (i.e., the size of the lattice)
b	Size of a lattice site
z	Lattice layer considered, independently of the lattice geometry
K	Number of nearest micelles from a central one
n	Solvophilic block length
m	Solvophobic block length
χ_{ij}	Flory–Huggins interaction parameter between segments i and j , with $\{i, j\} = \{A, B, G, W, C\}$, where C is a lattice site belonging to the colloidal particle
R_h	Hydrodynamic radius of a micelle
$\bar{\alpha}, \bar{\rho}$	Auxiliary functions used for evaluating R_h
ϕ_p^{bulk}	Micelle-forming polymer bulk concentration
ϕ_G^{bulk}	Guest (homo)polymer bulk concentration
ϕ_G^*	Guest (homo)polymer overlap concentration
g_p	Aggregation number of amphiphilic molecules in a micelle; the number of building blocks (unimers) per micelle
R_g	Radius of gyration of a homopolymer in solution
v_G	Volume of the guest homopolymer added to a colloidal suspension
h	Distance between two flat surfaces
$\Delta\chi$	Effective affinity surface–polymer
m	Shape parameter of a superball, $m = 2$ corresponds to a sphere and $m = \infty$ to a cube

$f(m)$	Function defining the volume of a superball
r	Maximum distance from the centre of a superball
s_c	Surface area of a colloid
c_c	Surface-integrated mean curvature of a colloid
r	Maximum distance from the centre of a superball
γ	Asphericity parameter
$\mathfrak{D}, \mathfrak{R}, \mathfrak{S}$	Functions of γ used for the EOS of <i>convex</i> particles
V_f	Volume that a colloid explores within the UC without overlapping with others
V_{UC}	Volume of the crystalline unit cell
$A \equiv L/\sigma$	Aspect ratio of a cylinder, with L its length
ρ_c	Number density of colloid
ρ_d^R	Number density of depletants in bulk
\tilde{z}	Depletant fugacity
\mathfrak{C}	Number of components in a system
G_P	Parsons–Lee scaling factor
\parallel	Parallel to the columnar direction vector (i.e., intra-columnar direction)
\perp	Perpendicular to the columnar direction vector (i.e., inter-columnar direction)
r_{\parallel}	Intra-columnar direction
r_{\perp}	Inter-columnar direction
g_{\perp}^{i-j}	Distribution function of particle-pair $\{i,j\}$ in r_{\perp} , with $\{i,j\}$ the colloid (c) or depletant (d)
$g_{\parallel}^{c-c,00}$	Colloid–colloid distribution function in r_{\parallel} for colloids within the same column
$g_{\parallel}^{c-c,01}$	Colloid–colloid distribution function in r_{\parallel} for colloids in different columns
Δ_{\perp}	Spacing between platelets in r_{\perp}
Δ_{\parallel}	Spacing between platelets in r_{\parallel}
ϕ_c^{\parallel}	ϕ_c from which depletion zones start to overlap in r_{\parallel}
ϕ_c^{\perp}	ϕ_c from which depletion zones start to overlap in r_{\perp}

Acronyms

ACPM	Association colloid–polymer mixture
AOV	Asakura–Oosawa–Vrij
C	Columnar phase
CEP	Critical end point
CMC	Critical micelle concentration
cp	Close packing
CP	Critical point

CPM	Colloid–polymer mixture
CS	Carnahan–Starling EOS
EOS	Equation of state
F	Colloidal fluid phase
FCC	Face-centred cubic crystalline phase
FMSA	First-order mean spherical approximation
FVT	Free volume theory
G	Colloidal gas phase
HS	Hard sphere
I	Isotropic phase
L	Colloidal liquid phase
LJD	Lennard-Jones-Devonshire EOS
N	Nematic phase
ODF	Orientation distribution function
PHS	Penetrable hard sphere
QP	Quadruple point
R	FVT reservoir of depletants
S	System of interest
SC	Simple cubic crystalline phase
SCF	Self-consistent field, used here to refer to the Scheutjens–Fleer SCF theory
SPT	Scaled particle theory
TP	Triple point
UC	Unit cell of a crystalline structure
VL	Vliegenthart–Lekkerkerker criterion