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Aggregation of solid microparticles at liquid-gas interface

Theses of Ph.D. dissertation

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1. The significance of the topic, scientific antecedents, and the definition of the goals

During two-dimensional aggregations solid micro-particles or clusters of particles, due to an interaction, stick together in a reversible or irreversible fashion at the interface between two different phases. The phenomenon can be a model for general growth problems, phase transitions, formation of particle associates, thermodynamics of interfaces, and also the formation of fractal patterns. Practical applications include thin-layer technology, and the description of the wettability of interfacial particles.

The interfacial aggregation of solid micro-particles was always in the centre of interest among researchers. Numerous obstacles had to be overcome due to the lack of quantitative measures describing the structure of aggregates. The development of this scientific field was greatly hastened by the discovery that the structure of interfacial aggregates can be characterised by fractal geometry introduced by B. B. Mandelbrot. Fractal geometry not only describes the structure of an aggregate, it also gives an insight into the mechanisms that created the pattern.

The most effective and most widely used methods in the study of interfacial aggregation phenomena are computer simulations. To avoid the need for large storage systems and long running times, most of these simulations use Monte-Carlo methods, that is, the clusters are joined into groups by predefined selection methods, they are aligned by an algorithm, and than treated as one cluster. This simulation method cannot be directly used for dynamical and kinetic analysis, no information can be gained on the process of the aggregation. The other possible way of simulating interfacial aggregations is the molecular dynamics approach, in which the motion of aggregating particles is governed by dynamic equations.

The main goal of this work is to gain new knowledge on the time evolution of interfacial (2D) aggregations, on the structure of the forming aggregates, and on the role of different properties of the primary particles. To achieve this goal I have investigated the aggregation of spherical and rod shaped particles at liquid-air interfaces, in different sub phases. With the aid of digital image analysis and self-developed software, I have characterised the structure of the aggregates, the kinetics and the dynamics of the aggregation process. In the first phase of my work I have compared the methods describing the structure of aggregates and assessed their credibility. For better interpretation of the results obtained on physical systems, I have created an aggregation model based on molecular dynamics, that makes the computer simulation of the two-dimensional aggregation of spherical and rod shaped particles possible. The simulation program based on this model can faithfully show the motion of the observed particles, thus it can be used for the visual, structural, kinetic, and dynamic analysis of the aggregation. I have made intensive computer simulation studies using this model.

2. The employed investigative tools

I have used the following materials for the physical experiments: SUPELCO silica spheres 75 ± 5 μm of diameter (ρ=2500 $\frac{kg}{m^3}$); polydisperse, rod-like carbon particles of 50-500 μm length, 35 ± 5 μm width (ρ=1240 $\frac{kg}{m^3}$); distilled water; 1:2 solution of glycerine (87%, Reanal, A.R.) and distilled water; 0.06 $mól/dm^3$ solution of NaDS (ionic surfactant) in water (Reanal, purum); $2g/100ml$ solution of Triton X-100 non-ionic surfactant and distilled water. For all fluids used I have obtained the surface tension using the Wilhelmy-plate method, and the dynamic viscosity by capillary viscometer.

I have set the wettability of the surface of the silica beads used in the physical experiments by silylation, using trimethylsilyl N,N-dimethylcarbamate dissolved in n-hexane. I have characterized the hydrophobicity of the surface-treated beads by their contact angle for the liquid. I have determined the wettability of the carbon particles by assessing the surface tension of the alcohol-water solution in which it sunk (critical surface tension), and described their electric properties by microelectrophoresis.

For recording the motion of monodisperse, aggregating silica spheres, I have used a black and white CCD camera. I have documented the behaviour of the polydisperse, aggregating carbon particles with a flatbed scanner. I have used digital image enhancing utilities to improve the quality of the recorded patterns. To derive the significant parameters that characterise the aggregation I have used a self-developed computer software.

I have investigated the aggregation model by using a simulation program developed by the Department of Physical Chemistry.

3. New scientific results

1. I have developed a computer software based on molecular dynamics, that allows the identification of correlated objects by any number of coordinative shells and also allows for the calculation of their characteristic parameters (e.g. radius a gyration, particle density, number of particles, anisotropy, etc.).

2. I have compared single object fractal dimension (D_f) measuring methods (box counting, correlation function, sand box method) by applying them to computer generated, uniformly structured patterns, and to real heterogeneous patterns. The comparison brought me to the conclusion, that the more heterogeneous the pattern is - the more different fractal structures it incorporates - the more the results of different D_f measuring methods diverge.

3. I have also compared series methods of fractal dimension determination, namely the radius of gyration (growth function) method and the geometric mean method, and found that the later consistently gives lower D_f. Based on these observations I have concluded, that the geometric mean method is more reliable if applied to anisotropic clusters. I have also found that the sand box and the correlation function methods give more precise values of D_f than the box counting method.

4. I have created a computer model based on molecular dynamics, that is an adequate tool for investigating the two-dimensional aggregation of spherical and anisotropic (rod shaped) particles. The novelty of my model is that it features long- and short-range interactions among the particles. With the aid of the model two-dimensional aggregation processes can faithfully be visualised and recorded, so it provides the possibility of structural, kinetic, and mechanism analysis of the aggregation. By comparing the results of real and simulated experiments I have found they show a good correlation, indicating the applicability of the model.

5. The results of real and simulated experiments showed that the first part of the interfacial aggregations - just like three-dimensional aggregations - have second order reaction kinetics, irrespective of the wettability of the particles. By comparing the kinetic curves of systems of different wettability I have found that in the case of weak wetting the curves are steeper - the value of the kinetic constant is greater - due to the greater capillary attraction induced by the greater contact angle.

6. The analysis of the kinetic curves resulted in the observation, that in the second part of the aggregation process, the driving force of the aggregation is greater or increasing. Judged by the simulated experiments the reason for this is that growing clusters experience growing capillary attraction that cannot be compensated for by the also growing hydrodynamic resistance.

7. I have shown that short-range forces - through the restructuring of the clusters - have an indirect effect on the aggregation kinetics. With the aid of computer experiments, I have shown that this effect of the short-range forces becomes relevant only in the case of large aggregates.

8. Through real and simulated experiments I have found a correlation between the driving force of the aggregation and the polydispersity of the system, that is greater driving force of the aggregation results in lower polydispersity. The reason for this is that greater driving force (strong capillary attraction) produces more small clusters that can grow, thus the growth process becomes more uniform, resulting in lower polydispersity.

9. The fractal dimension values obtained by the series method on systems of carbon particles and systems of silica spheres of medium and high hydrophobicity show no significant differences, indicating that the shape, the polydispersity, and the wettability of the primer particles have no effect on the fractal geometry. I have made the same observation by calculating the dependence of the effective fractal dimension of the clusters (using single object measuring techniques) on the size of the clusters. This is yet another proof of the theory of universality.

4. Publications

Papers

[1] R. Fata, A. Vincze, J. Kertész, M. Zrínyi and Z. Hórvölgyi: Two-dimensional aggregation of silanized microbeads: a kinetic study, Proc. of 7^{th} Conference on Colloid Chemistry (Eds.: Z. Hórvölgyi, Zs. Németh and I. Pászli), Hungarian Chemical Society, Budapest, Hungary, 60-63 (1997)

[2] A. Vincze, J. Kertész, M. Zrínyi and Z. Hórvölgyi: The structural analysis of two-dimensional aggregates composed of cylindrical microparticles, Proc. of 7^{th} Conference on Colloid Chemistry (Eds.: Z. Hórvölgyi, Zs. Németh and I. Pászli), Hungarian Chemical Society, Budapest, Hungary, 196-199 (1997)

[3] A. Vincze, R. Fata, M. Zrínyi, Z. Hórvölgyi and J. Kertész: Comparison of aggregation of rod-like and spherical particles: A fractal analysis, J. Chem. Phys., 107(18), 7451-7458 (1997)

[4] A. Vincze, M. Zrínyi, Z. Hórvölgyi: Particle size analysis by computer, Proc. of PORANAL 98, Eger, Hungary, 83 (1998)

[5] A. Vincze, M. Zrínyi, Z. Hórvölgyi: Computerized analysis of two-dimensional aggregates (in Hungarian), Proc. of PORANAL 98, Eger, Hungary, 85-92 (1998)

[6] A. Vincze, R. Fata, Gy. Parlagh, M. Zrínyi, J. Kertész, Z. Hórvölgyi: Kinetic and structural study of interfacial aggregation of microparticles at liquid-air interfaces, Periodica Mathematica Hungarica, 37 (1-3), 207-215 (1998)

[7] A. Agod, A. Vincze, J. Kertész, M. Zrínyi, Z. Hórvölgyi: Simulation of aggregation in two dimension (in Hungarian), Proc. of Vegyészkonferencia '99 (Erdélyi Magyar Műszaki Tudományos Társaság), Kolozsvár, Románia, 24-27 (1999)

[8] A. Vincze, M. Zrínyi, Z. Hórvölgyi: Characterization of particle shape and particle sizes by computer (in Hungarian), Proc. of Műszaki Kémiai Napok 2000 (Ed.: J. Filka), KE Műszaki Kémiai Kutató Intézet, Veszprém, Hungary, 107-108 (2000)

[9] A. Agod, A. Vincze, J. Kertész, M. Zrínyi, Z. Hórvölgyi: Mechanism of aggregations and the cluster size distributions (in Hungarian), Proc. of Vegyészkonferencia 2000 (Erdélyi Magyar Műszaki Tudományos Társaság), Kolozsvár, Románia, 85-90 (2000)

[10] A. Vincze, A. Agod, J. Kertész, M. Zrínyi and Z. Hórvölgyi: Aggregation kinetics in two-dimension: Real experiments and computer simulations, J. Chem. Phys., 114(1), 520-529 (2001)

[11] A. Vincze, L. Demkó, M. Vörös, M. Zrínyi, M. N. Esmail and Z. Hórvölgyi: Two-dimensional aggregation of rod-like particles: a model investigation, J. Phys. Chem. B, 106, 2404-2414 (2002)

Lectures

[1] M. Fata, A. Vincze, J. Kertész, M. Zrínyi and Z. Hórvölgyi: Two-dimensional aggregation of silanized microbeads: a kinetic study, 7^{th} Conference on Colloid Chemistry, Eger, Hungary, Abstr. L61 (1996)

[2] A. Vincze, J. Kertész, M. Zrínyi and Z. Hórvölgyi: The structural analysis of two-dimensional aggregates composed of cylindrical microparticles, 7^{th} Conference on Colloid Chemistry, Eger, Hungary, Abstr. L26 (1996)

[3] A. Vincze, R. Fata, Gy. Parlagh, M. Zrínyi, J. Kertész, Z. Hórvölgyi: Kinetic and structural study of interfacial aggregation of microparticles at liquid-air interfaces, Conference on Dimensions and Dynamics, Miskolc, Hungary (1998)

[4] A. Vincze, M. Zrínyi, Z. Hórvölgyi: Computerized analysis of two-dimensional aggregates (in Hungarian), PORANAL 98, Eger, Hungary, Proc. (1998)

[5] A. Vincze, M. Zrínyi, Z. Hórvölgyi: Particle size analysis by computer, PORANAL 98, Eger, Hungary, Proc. (1998)

[6] A. Agod, A. Vincze, J. Kertész, M. Zrínyi, Z. Hórvölgyi: Modelling of interfacial aggregation phenomena (in Hungarian), Műszaki Kémiai Napok '99, Veszprém, Hungary, Proc. (1999)

[7] A. Agod, A. Vincze, J. Kertész, M. Zrínyi, Z. Hórvölgyi: Simulation of aggregation in two dimension (in Hungarian), Vegyészkonferencia '99, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, Románia, Proc. (1999)

[8] A. Vincze, M. Zrínyi, Z. Hórvölgyi: Characterization of particle shape and particle sizes by computer (in Hungarian), Műszaki Kémiai Napok 2000, Veszprém, Hungary, Proc. (2000)

[9] A. Vincze, A. Agod, J. Kertész, M. Zrínyi, Z. Hórvölgyi: Interfacial aggregation of spherical microparticles: computer simulations and real experiments, 3^{th} European Conference on Computational Chemistry, Budapest, Hungary, Abstr. O-17 (2000)

[10] A. Vincze, L. Demkó, M. Vörös, J. Kertész, M. Zrínyi, Z. Hórvölgyi: Interfacial aggregation of rod-like particles: computer simulations and real experiments, 3^{th} European Conference on Computational Chemistry, Budapest, Hungary, Abstr. P4-25 (2000)

[11] A. Agod, A. Vincze, J. Kertész, M. Zrínyi, Z. Hórvölgyi: Mechanism of aggregations and the cluster size distributions (in Hungarian), Vegyészkonferencia 2000, Kolozsvár, Románia, Proc. (2000)