Spring Semester 2022

DYNAMICS OF COMPLEX FLUIDS

MSE 583

Instructor: Professor Ken Schweizer, kschweiz@illinois.edu , 206 MSEB

Time & Place: 9:30-10:50 am Tuesday & Thursday 4101 MSEB

This course is an intermediate-level introduction to the ***fundamental physical aspects (basic science)*** *of the dynamics, viscoelasticity and mechanical response of polymers and colloids in the liquid state. The formation of nonequilibrium colloidal physical gels and glasses is also discussed, as is briefly the rheology of particle gels. An overarching theme is to understand the microscopic connections between colloidal particle or polymer architecture, intermolecular forces, collective fluid structure, and time-dependent phenomena. Experimental behavior and theoretical concepts are presented in an integrated manner.*

This course is not about continuum mechanics nor hydrodynamics, detailed discussion of the equilibrium behavior of colloids or polymers, engineering applications, or biological systems (though the material is germane to biophysics and biomaterials in a general soft matter sense). There are other courses on these subjects. The emphasis is on the basic physics, models and ideas, including general aspects and phenomena influenced by tunable structure and interactions.

Topics covered fall into 3 main categories:

* GENERAL ASPECTS of COMPLEX FLUIDS: Fickian Diffusion, Relaxation, Mechanical Response, Flow, Maxwell Model, Colloidal Forces, Structural Pair Correlation Functions, Scattering Structure Factors, Brownian Motion, Hydrodynamics (briefly), Langevin Equation, Time Correlation Functions, Generalized Langevin Equation

* COLLOIDAL and NANOPARTICLE SUSPENSIONS: Diversity of Tunable Forces, Liquid Structure, Fickian and non-Fickian Diffusion, Viscoelasticity, Caging, Glass Transition, Aggregation, Percolation, Gelation, Yielding

* POLYMER LIQUIDS: Elementary Statistical Chain Models, Dense Melts, Metrics of Coil Interpenetration, Unentangled and Entangled Dynamics, Diffusion, Dielectric Relaxation, Viscoelasticity, Rouse Model, Reptation/Tube Model, Alternative Relaxation Mechanisms, Other Architectures (star branched, rings, rigid rods)

BOOK REFERENCES

Primary "Texts"

R.G.Larson, "Structure & Rheology of Complex Fluids" **Larson**

This book is modestly useful for both the colloid and polymer topics

M.Rubinstein & R.H.Colby, "Polymer Physics" **RC**

*This book is **excellent** for all polymer topics*

More Specialized Useful Books (in Grainger library on reserve)

W.Russel, D.Saville & W.Schowalter, "Colloidal Dispersions" **RSS**
R.J.Hunter, "Foundations of Colloid Science", volume 1 **Hunter**
M.Doi & S.F.Edwards, "Theory of Polymer Dynamics" **DE**

Basic Statistical Mechanics Texts

D.McQuarrie, "Statistical Mechanics" **McQ**
D.Chandler, "Introduction to Modern Statistical Mechanics" **DC**
J.P.Hansen and I.R.MacDonald, "Theory of Simple Liquids" **HM**

Logistics

All homework sets & answers, PDFs of lecture & vugraph slides, and any other course material is sent directly by email attachment. There is no TA and no specific office hours. I am available by email and 1-on-1 meetings if you have questions not asked in class. I generally respond very promptly.

Note: In pre-pandemic days the class was taught using a blackboard with students required to take notes. You now will have my notes on the slides I will use to lecture. Hence, except for writing down a few things I say not on the slides that you feel are important, you do not need to take notes. *This allows the class to ask more questions. Please participate.* ***Lectures will not be recorded, and attendance in class is expected.***

Exams

Grading: based on two in-class, 80 minute exams.
One on Part I of the course, a 2nd on Part II. Each mid-term will count 50% of your grade.

1st Exam ~7-10 days after we finish last class on Part I. Likely March 22.
2nd Exam on last day of class, May 4.

Homework

Given roughly once every 2 weeks. Working hard on the problem sets is the best way to learn the material and prepare for exams. It will not be collected nor graded (there is no TA). I will send you detailed solutions. I *strongly* suggest you initially *independently* work on the homework. After sufficient effort, discussing the problems with other students can be useful, as is then looking at the answers I send you. If you then have any questions, please contact me.

MSE 583 COURSE OUTLINE (2022)

Numbers in parentheses = estimated number of lectures
Book references defined above are given for each sub-topic.

PART I. GENERAL TOPICS & COLLOIDAL SUSPENSIONS (7 ½ weeks)

A. Introduction / Generic Basic Concepts (5)

* Survey of experimental phenomena
* Basics of diffusion, mechanical response, viscoelasticity
* Brownian motion / Langevin Equation / Time correlation functions
* Hydrodynamics / Stokes-Einstein relation (*brief*)

Larson, ch.1.1-1.4 ; DE, ch. 3
RSS, ch. 1,2.6, 3.1-3.3; Hunter ch.1,2; McQ ch. 20,21; HM, ch. 7

B. Intermolecular Forces, Structure & Phase Behavior (3)

* Atoms versus Colloids
* Tunable Forces: Excluded volume, van der Waals, Coulomb, Gravity
* Phase Behavior
* Liquid Structure: pair correlations, scattering profiles

Larson, ch. 2.1-2.4, 7.2
RSS, ch. 4,5, 10 ; Hunter, ch. 4,6,7 ; McQ, ch.13, 22 ; HM, ch. 1,5 ; DC, ch. 8

C. Equilibrium Dynamics of Stable Suspensions (3)

* Interactive Brownian motion; Many particle hydrodynamics (*brief*)
* Experimental behaviors
* Intermediate concentrations; Binary collisions ideas
* Dense repulsive colloid suspensions ; Caging ; Viscoelasticity
  dynamic light scattering and structural relaxation

Larson, ch. 6.1-6.4, 7.2
RSS, ch. 13, 14; Hunter, ch.9; HM, ch. 9

D. NONequilibrium Processes (4)

* Glassy dynamics & vitrification; Generalized Langevin equation; Experiments;
  Modern theoretical concepts; Shear thinning
* Adhesive (sticky) colloid dynamics, physical bonds, percolation, gelation, yielding

Larson, ch. 7.2, 7.3 ; RSS , ch. 14

PART II. POLYMER LIQUIDS (5 ½ - 6 weeks)

A. Chain Conformation and Liquid Structure (2)

* Chemical vs. Coarse-grained statistical descriptions
* Gaussian bead-spring model
* Conformation and structure in dense melts
* Relationship between chemical structure and coil interpenetration
  Packing length concept and geometric meaning

RC ch. 2-5; Larson, ch. 2.2, 3.1, 3.2; DE, ch. 1,2

B. Single Chain Brownian Dynamic Theories and Unentangled Melt Dynamics (4)

* Langevin equations in short chain unentangled melts
* Rouse model; Segmental friction
* Self-diffusion, viscosity, stress relaxation, dielectric relaxation

RC ch. 8 ; Larson, ch. 3.3-3.6 ; DE, ch. 3,4

C. Entangled Polymer Melts (6)

* Survey of experimental phenomena for entangled chains
* Chemical crosslinks and entropic rubber elasticity
* Melt Entanglement plateau modulus and chemical structure
* Reptation/Tube model; predictions for diffusion, viscoelasticity, dielectrics…
* Experimental puzzles ; Additional non-reptation motions
* Nonlinear rheology (*very* brief introduction)
* Other Architectures: cyclic rings, branched stars, rigid rods

RC 7, 9 ; Larson, ch. 3.7 ; DE, ch. 6,7