Spring Semester 2024

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 structure, intermolecular forces, 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, the detailed equilibrium behavior of colloids or polymers, polymer solutions, engineering applications, or biological systems (though the material is germane to bio-systems in a general sense). There are many other courses on these subjects. The emphasis is on the basic physics, models and ideas, including general aspects and phenomena influenced by structure and interactions.* ***Moreover, the focus is on highly concentrated systems, both colloidal and polymeric.***

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 (very briefly), Langevin Equation, Time Correlation Functions, Microscopic Stress, Generalized Langevin Equation

* COLLOIDAL and NANOPARTICLE SUSPENSIONS: Tunable Repulsive and Attractive Interactions, Liquid Structure, Diffusion, Viscosity, Viscoelasticity, Collisions and Caging, Glass Transition, Aggregation, Percolation, Gelation, Yielding

* POLYMER LIQUIDS: Elementary Statistical Chain Models, Dense Melts, Metrics of Coil Interpenetration, Unentangled and Entangled Melt Dynamics, Diffusion, Dielectric Relaxation, Viscoelasticity, Rouse Model, Reptation/Tube Model, Alternative Relaxation Mechanisms, Other Architectures: Cyclic Rings, Star-Branched, 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 always available by email and for 1-on-1 meetings.

Note1: In pre-pandemic days the class was taught using a blackboard with students required to take notes. You now will get most (not all) of my notes on the slides I use to lecture. *This allows the class to ask more questions. Please participate.* Lectures will not be recorded, and attendance in class is expected. Some new topics have been added in 2024, and most will be presented using the blackboard, the old fashioned way. You are responsible for all such material. It is thus especially essential that you attend class and take notes as needed.

Note2: I will be out of town March 5 at the American Physical Society mtg. The March 5 lecture will be recorded and uploaded to MediaSpace. There are 2 possibilities for the mid-term exam date, see below. This will be determined later, in consultation with the class.

Note3: Spring break is week of March 11. No classes.

Exams

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

1st Exam on Part I on either **Thursday March 7** or **Tuesday March 19**
2nd Exam on Part II per the campus schedule during finals week

Homework

Given roughly once every 2 weeks. Working hard on the problem sets is one of the best ways to learn the material and prepare for exams. It will not be collected (there is no TA). I will send you detailed solutions. I *strongly* suggest you initially *independently* work on the homework. After sufficient effort, discussing with other students is useful and looking at the answers I send you is appropriate. If you have any questions, I am happy to meet and discuss.

MSE 583 COURSE OUTLINE (2024)

Numbers in parentheses = estimated number of lectures

Book references defined above are given for each sub-topic.

*New Topics / Changes in 2024 are indicated in blue. The associated material will **NOT** be in the distributed lecture slides but rather presented on the blackboard, so you are expected to take notes in real time as explained above.*

PART I. GENERAL TOPICS & COLLOIDAL SUSPENSIONS (6 ½ weeks…13 classes)

A. Introduction / Generic Basic Concepts (5)

* Introductory qualitative survey of basics of experimental phenomena of entire course
* Basics of self-diffusion, mechanical response, viscoelasticity
* Brownian motion / Single particle hydrodynamics (Stokes-Einstein relation)
* Langevin Equation / Time correlation functions / Velocity Autocorrelation Function (VACF), Mean Square Displacement (MSD)
* Microscopic stress, stress relaxation function, Green-Kubo relation for viscosity

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 Interactions and Forces (1)

* Tunable Forces: Excluded Volume, Coulomb Repulsion, van der Waals Attraction
  Effective hard sphere paradigm for repulsive colloids

Larson, ch. 2.1-2.4, 7.2
RSS, ch. 4,5, 10 ; Hunter, ch. 4,6,7

C. Equilibrium Dynamics of *Dense* Stable Suspensions of Repulsive Colloids (3)

* Interactive Brownian motion at intermediate and high concentrations
  Liquid Structure: pair correlation function g(r), scattering structure factor S(k)
  Experimental behavior with focus on high concentrations

* Binary Collisions, Many Particle Dynamic Caging, Fluids vs Suspensions
  2 dynamical regimes concept (short and long time processes), VACF, MSD

* Molecular Viscoelasticity, Diffusion, Structural Relaxation
  Introduction to modern theory: Force-Force Time Correlations, Structure-Dynamics-Viscosity Connection, Cage vs Self Diffusion
  Intuitive criterion for shear thinning: effective Peclet number

Larson, ch. 6.1-6.4, 7.2
RSS, ch. 13, 14; Hunter, ch.9; HM, ch. 9
McQ, ch.13, 22 ; HM, ch. 1,5 ; DC, ch. 8

D. NONequilibrium Processes: Colloidal Glasses and Gels (4)

* Slow glassy dynamics & vitrification at ultra-high volume fractions in dense repulsive colloid suspensions; Generalized Langevin Equation

* Modern theoretical concepts: transient cage localization, shear elasticity, self-consistent treatment of force time correlations and long time diffusion and flow
amorphous solid like activated hopping transport; Kramers barrier crossing

* Attractive colloid dynamics, physical vs chemical gels, physical bonds and geometric percolation, kinetic gelation criteria, activated bond breaking dynamics (Kramers)

* Deformation-induced solid-to-liquid transition; Yielding as a Force Imbalance

Larson, ch. 7.2, 7.3 ; RSS , ch. 1

PART II. POLYMER LIQUIDS (7 ½ weeks….15 classes)

A. Background: Chain Conformation and Liquid Structure in Melts (2)

* Coarse-grained description, concept of statistical segment, Gaussian bead-spring model, Conformational statistical structure

* Relationship between chemical structure and coil interpenetration
Packing length concept, geometric meaning, experimental behavior

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

B. Single Chain Brownian Dynamic Theory & Unentangled Melt Dynamics (5)

* Rouse Model: coupled Langevin equations for short chain melts; physical assumptions, segmental friction and vitrification, time-temperature superposition concept

* Rouse Model Analysis: Mathematical Solution, Rouse Modes, Time Correlations, Core Results, Relation to Observable Properties

*Rouse Model Analysis: Dynamic Scaling Solution (Rubinstein-Colby book approach)

** Comparison to Experiments on Unentangled Polymer Melts:
center of mass self-diffusion, segmental diffusion, end-to-end vector relaxation, dielectric relaxation, viscosity, stress relaxation in time and frequency space

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

C. Entangled Chain Polymer Melts (5 ½)

* Survey of experimental phenomena; chemical crosslinks and entropic rubber elasticity; perceptions of entanglements, melt entropic entanglement plateau modulus and chemical structure dependence

** Reptation/Tube model: Physical Ideas, Dynamic Scaling Approach, Tube survival function, Rouse dynamics along 1D curvilinear path in the tube

** Predictions for diffusion constant, segmental and center-of-mass MSD, viscoelasticity, Dielectrics ; Comparison to Experiment, Successes and Failures

* Non-Reptation motions: Contour Length Fluctuations, Constraint Release; Experiments

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

D. Beyond Linear Chains: Other Macromolecular Architectures (2 ½)

*Cyclic Rings: complicated experimental history; collapsed fluctuating globule conformation (connection to chromosomes?), "normal" dynamical/viscoelastic regime; emergence of macromolecular "topological" glass?

*Star-Branched: entanglements, tubes, activated arm retraction model; exponentially slow dynamics

*Rigid Rod Solutions: entanglements, tube/reptation model; decoupling of diffusion, orientational/rotational relaxation & flow

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