Chemistry 567: *Chemical Kinetics*

This syllabus was last updated January 4, 2010 and is subject to change (for the better, we hope!)

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1. Principal Goals of the Course

Chemistry is inherently a dynamical science—things change. Without chemical reactions, chemistry loses its beauty and significance. Most of what you have studied in previous courses has imagined that what matters most is the equilibrium properties of, for example, reactants and products. There are two basic reasons for this focus: (1) equilibrium considerations are indeed important, and (2) it is very difficult to understand chemical phenomena away from equilibrium. Thus it would seem convenient that equilibrium properties are capable of capturing key chemical information while enabling useful predictions.

Nevertheless, we must believe it to be important that time passes during every chemical transformation. The question arises: how do we put "time" into chemistry? This course will attempt to answer that question using a combination of lectures, discussion, and projects. We will spend time both on formal theory (equations, derivations, models and approximations) and on practical implementation (computer simulations and discussions of experiments). My main goal is to help you to feel comfortable putting the variable '*t*' back into your chemical thinking, which for the most part has only included that variable in the context of simple kinetics.

We will base the structure of the course around the main computer simulation projects that we will be using. I will list them as follows:

1. Diffusion

2. The Langevin Equation and the Kramers Problem

3. Monte Carlo Simulation of Kinetics

4. Realistic Molecular Dynamics Simulation: Water and Beyond

5. Quantum Dynamics: Unitary Evolution (a test of time-dependent perturbation theory)

6. Quantum Dynamics: Finding the Ground State Wavefunction

7. Quantum Relaxation Dynamics: The Redfield Equation

Throughout the course, we will look at computer simulations to illustrate and animate lecture and discussion topics.

2. Predicted Schedule

Key: McQ = McQuarrie, *Statistical Mechanics*; H = Houston, *Chemical Kinetics and Reaction Dynamics*; IMSM = Chandler, *Introduction to Modern Statistical Mechanics*; Mess = Messiah, *Quantum Mechanics*; Muk = Mukamel, *Principles of Nonlinear Optical Spectroscopy*.

Items in **bold** are computer simulation assignments. All the assignments in the course will be based on these simulations. The final paper is a research proposal that describes how experimental and computational methods will be used to study one specific chemical process. The final paper is due **Wednesday, April 28, 2010**; this is the day our exam would have been if there was an exam. I am expected to submit grades within 72 hours of this date, so there is not much flexibility, if you want a grade, please submit your paper! You may submit your paper and all assignments electronically through the ctools site.

Date	Topic	Notes
1/6/09	Intro discussion	**Diffusion sim**
1/8/09	Diffusion and the Langevin Equation	McQ (Ch. 20); H (Ch. 4)
1/11/09	Correlation functions/linear response	McQ (Ch. 21-22); IMSM (Ch. 8)
1/13/09	Correlation functions/linear response	McQ (Ch. 21-22); IMSM (Ch. 8)
1/15/09	Kramers Problem	H (Ch. 5) **Kramers sim**
1/18/09	No class (MLK holiday)	
1/20/09	Single Molecule Chemistry	Paper
1/22/09	A Step Back: Collision Theory	H (Ch. 3)
1/25/09	A Step Back: Potential Energy Surfaces and Transition State Theory	H (Ch. 3)
1/27/09	Detailed Balance and Chemical Exchange	**Monte Carlo sim** and Paper
1/29/09	*gap to allow for some slack*	
2/1/09	Marcus theory of electron transfer	H (Ch. 5) + extra
2/3/09	Marcus theory of electron transfer	H (Ch. 5) + extra
2/5/09	Proton transfer and PCET	Paper

Date	Topic	Notes
2/8/09	Molecular dynamics	R (various); **MD water sim**
2/10/09	Ultrafast spectroscopy	H (Ch. 7)
2/12/09	Photochemistry (kinetics)	H (Ch. 7)
2/15/09	Solvation dynamics	H (Ch. 7)
2/17/09	*gap to allow for some slack*	
2/19/09	Coupled quantum oscillators	Mess (Ch.VIII) and Muk (Ch. 2); **Unitary evolution sim**
2/22/09	Time dependence in quantum mechanics	Mess (Ch.VIII)
2/24/09	Time-dependent Hamiltonian	Mess (Ch.VIII); Muk (Ch. 2)
2/26/09	Quantum double-well	**Finding the ground state wavefunction**
3/1/09	Spring Break	
3/3/09	Spring Break	
3/5/09	Spring Break	
3/8/09	Time-dependent perturbation theory	Muk (Ch. 2); Mess (Ch. XVII); discuss proposal topic
3/10/09	Density operator	Mess (Ch.VIII, sect. 21-25)
3/12/09	Quantum dynamics in Liouville space	Muk (Ch. 3)
3/15/09	Reduced density operator	
3/17/09	Redfield theory	**Redfield sim**
3/19/09	Redfield theory	
3/22/09	ACS Meeting	Paper: Anna
3/24/09	ACS Meeting	Paper: Baiz
3/26/09	Linear response theory	**Linear response MD sim**
3/29/09	Examples of linear response	
3/31/09	Nonequilibrium biochemistry: pumps	Astumian papers

Date	Topic	Notes
4/2/09	Nonequilibrium biochemistry: pumps	Astumian papers
4/5/09	Jarzynski equality: relationship between non equilibrium and equilibrium stat mech	Szabo paper
4/7/09	Experimental methods: pump-probe and time resolved fluorescence	
4/9/09	Case study: natural photosynthesis	
4/12/09	Case study: GFP proton transfer	Papers: Boxer; Matthies
4/14/09	Case study: excited state charge transfer	Papers: Baiz
4/16/09	Discussion	
4/19/09	Discussion	

3. Assignments

The best way to learn anything is by teaching it, and that is my goal is for myself in this course. The next best way to learn something is to use it. So rather than scribble reams of notes and deriving lots of equations, you will scribble notes and then *use* the results in your assignments. We will use many concepts that you will already have seen in other courses—especially quantum mechanics and statistical mechanics. It is possible that you will understand those concepts better after using them in this course.

The assignments in this course have come from calculations and simulations that I have developed for myself to understand fundamental aspects of the kinds of chemical processes that I study with my research group. I have also developed these exercises for my version of Chem 571. For this course, some of the inspiration has come from materials used in an undergraduate course at UM called Chem 462: Computational Chemistry. But I have made substantial modifications (and so will you) to take the level well beyond what any undergraduate would see.

General Structure

Mostly the assignments will break down into three thematic sections. They are as follows:

1. Code modification:
    a. add or modify some section of the code to make the program functional (they will not function out-of-the-box)
    b. add a new functionality that the program did not have initially
2. Data collection: running the program and collecting "data"
3. Extracting the science: making observations about the computer data

For each section, you will be asked to remark on what you have done, why you did it, what the result was, and what it means. Many of the questions will be open-ended, and may not have formally correct answers. It is my goal to make these assignments seem more like real science than like jumping through hoops. It will be hard to make the programs run and produce meaningful results if you do not understand the physical science principles that underlie the programs.

I have no idea how hard these assignments will be, so there will be some leniency in due dates, but I do want everyone to finish them, so please do not start them the night before. There will be a learning curve for most students, regardless of your familiarity with programming. In fact, I sincerely hope that programming is not a central focus in these exercises.

Team Work

Science is not typically done alone, and I encourage team work. Brainstorming is also team work, but writing is not. I would thus ask that all assignment write-ups be written alone. It is natural that your write-up will include ideas and insights from your other team members, and for that reason please state at the beginning the other class members you worked with.

Writing

Physical chemistry may be the most abstract branch of chemistry. Although many think of it to be the most precise, we often make molecular interpretations based on analogy or using idealized models whose validity is not always obvious. In my personal view, physical chemistry is an impressionistic science, where we only see vague forms of the molecules we are studying, particularly in comparison to the certainty of analytical methods that are generally focused on counting things, or synthesis where one is rewarded with a structure at the end of the hard work. To convert a few wiggles of a spectrum into a molecular story takes work, insight, and guts. Getting the message out requires communication skills that rise to the challenge. Scientific results that are not communicated do not exist, and results that are described poorly will not carry the same weight as those that are presented clearly and convincingly. It is important to keep in mind that much of scientific writing is persuasive writing, although one must always strive to present all evidence and arguments—both those in favor and opposed to your conclusions. The line is fine between detached descriptive writing (probably like the bland verbiage of most lab reports) and over-the-top marketing. I would like your assignment reports to read like a research article, like one in a journal like *J. Phys. Chem.* or *J. Am. Chem. Soc.*

For your final paper, you will write a research proposal. Other specialties in this department have a research proposal as a candidacy requirement. Since we do not have this requirement in physical chemistry, I think you would do well to practice this altogether different writing style. Any job you are likely to apply for—whether a postdoctoral fellowship, junior faculty position or a position in a company—will require you to devise a convincing proposal of an unanswered question, what is known about it, and how you can address the question. The writing style for a research proposal is quite different from a journal article, since you have no data, and you can only speculate on what you will see. Nevertheless, you identify questions (only **one** for this course) and devise a plan to study the question. You must also consider that there are many

other smart people submitting proposals and only a small amount of funding available, so you have to explain why your question is really important, and why your approach is the best way to answer your really important question. The style you are aiming for here is much more persuasive than in a paper, and it may border on becoming overbearing, but not too overbearing. If this sounds hard, you bet it is.

For the research proposal, I would like you pick something that really takes the material from the course rather than try to adapt what you have done or plan to do for your own research. To make sure this happens, and to help focus your thinking, I would like you to meet with me to discuss your proposal topic. I may guide you to a more narrow focus, or suggest something related that is more appropriate for the course. There is no length minimum or limit, but I would suggest that 7-10 single-space pages is a good target length. There should be figures and references in addition to the main text. A typical outline is as follows (in parentheses I have estimated page counts):

1. **Abstract** (< 500 words) Explaining the main question and what you plan to do. Think about an "airport seminar": how would you describe your project to a colleague during a brief encounter at an airport. What the funding agency program manager will say to his or her supervisor will likely be drawn from the abstract.
2. **Project Objectives:** (1 page) Lay out what you plan to study and your experimental and computational approach. Why is this project important to science? Does it address a societal need?
3. **Methods:** (1 page) Describe the methods you will use. You may put in an experimental diagram, but it is not necessary if the technique is clearly described. Emphasize the chemical information that the methods will enable you to extract. Do not make this section too long.
4. **Background:** (2-3 pages) What are the main things that are known about what you plan to study. It is important to stress often what is not known—especially the aspect you hope to study.
5. **Proposed Research:** (3 pages) Describe in detail what experiment you will do and what computational study you will do. Explain what you think will happen (or suggest possibilities), and what the interpretation would be for such outcomes. Describe one possible pitfall and how you will deal with it if it happens. Make sure to draw on the ideas you discussed in the background section, and how the new data and computations will provide new insight.

Hints for finding ideas: think of a subject that you like, find a review article about it, and look at the intro and the conclusion. The intro will summarize what is known and the conclusion will likely be a description of unanswered questions. Steal these! A great source of palatable and manageable reviews is *Accounts of Chemical Research* (an ACS journal).

When you meet with me to discuss your proposal, bring copies of key papers you have used to find your idea (you can also send them by email--I don't like paper).

4. Grading

There are 8 assignments which together will be worth 60% of the final grade. The final paper will be worth 40%. Please do your best to hand things in on time. I do not like nagging.

5. Computer "Programming"

MATLAB

While I do not particularly care what language the assignments are done in (besides English for the write-up!), I will be giving out lots of pre-written code in MATLAB, so I would suggest using MATLAB. There are many options for running MATLAB, you can buy a cheap student license at the computer store, you can use the Science Learning Center, or you can ask your research supervisor to use MATLAB on a lab computer (they can have it installed at no cost by the IT staff). MATLAB is pretty simple to use, with a very tolerant syntax and runs on all operating systems with no need to compile anything (so no need to learn UNIX stuff). I am happy to give help, where needed, but I will also provide links to tutorials that should be helpful. Everything except the "real" molecular dynamics simulation will be done in MATLAB (if you use the code I give you).

GROMACS

It stands for GROningen MAchine for Chemical Simulations and is a popular package to use when you want to compute explicit solvent molecular dynamics simulations, since the code is highly optimized. We will be using it for our realistic water simulation, and to show you how to setup a calculation and analyze the data. I have tried to keep most of the UNIX stuff to a minimum by writing all the scripts you will need to use (though, of course, you will need to modify them somewhere). It is hard to install GROMACS on most computers, so the class will be using machines in my research group remotely. I'm not exactly sure how we will organize this yet, but we'll figure it out. Incidentally, it is very easy to install GROMACS on any Mac or on any machine running Linux, but it is not easy to get it to work on Windows (especially since pretty much no one does MD simulations using Windows machines).