Chemistry 166

Nonequilibrium Statistical Mechanics

Tues & Th 9:00 – 10:25 a.m.
147 Noyes

Syllabus

The key to the references is given at the end of this syllabus.

1. *Introduction:* Remarks on kinetic theory, linear response theory and time correlation functions. Ref. 1-1, p. 357

2. *Elementary kinetic theory*: Number of collisions/area/time; approximate models for viscosity η, heat conductivity κ and self-diffusion *D*; Calculation of $\kappa M/\eta C_v$ and comparison with experiment and with more exact theory. Ref. Chaps. 16 (pp. 357-365); Re, Chap. 13A-13B; He, Chaps. 5.1 to 5.3 (up to p. 183), 5.4.

3. *Boltzmann equation, Collisions, and consequences*: Collisions, laboratory and center of mass systems of coordinates, impact parameter, differential scattering cross-section, rainbow angle; Boltzmann equation for time-dependent single particle distribution function *f*; Collision term in Boltzmann equation; Rate of change of the average of any collisional quantity $\phi(\mathbf{v}, \mathbf{r})$, particularly $\phi = 1n\ f$; *H*-theorem; Steady-state (it has no further increase of entropy); Collisional invariants; Systematic solution of the Boltzmann integro-differential equation for the distribution function; Expressions for fluxes energy, mass, momentum); Transport coefficients; Use of orthogonal polynomials. Ref. Chap. 19; He, Chap. 5.3.1 to 5.7; Hu, Chaps. 3.1-3.3, 5; K, Chap. 2.7-2.9, 9.4-9.5; Re, Chap. 13C-13D; W, Chap. in book cited in refs; Z, Chap. 5.

4. *Brownian Motion:* Brownian motion and history, 1827-1950s; Random variables, stochastic processes; Gaussian random variables and sum of g.r.v.; Brownian motion and diffusion; Langevin equation for particle under random and frictional forces; Displacement of *x* in time; Deduction of probability distribution $P(x, t \mid x_o)$; Estimate of the function coefficient ζ; Velocity autocorrelation function and diffusion, from solution of the Langevin equation; First fluctuation-dissipation theorem; Generalized Langevin equation (GLE); Langevin equation and GLE for harmonic oscillator; Correlation function $\langle x(t)\, x(0)\rangle$ for this harmonic oscillator, and its Fourier-Laplace transform. Liouville operator and applications. Ref. Chap. 20; F, Chap. 12; K, Chap. 8; K, Chaps. 1-1.2, 1.5; P, Chap. 6; Re, Chap. 15 F; Ha, Chap. 4.1-4.2; Ri, Chaps. 1.1, 3.1; L, Chap. 2-2.2; Z, Chaps. 2 and 3.

5. *Time-correlation Functions and Spectroscopy*:; Optical absorption and correlation function for transition dipole moment; Cumulant expansion and truncation to two-time

point correlation (Kubo); Role of modulation rate and magnitude in determining shape of optical absorption band (Gaussian, Lorentzian); Implementation of expression for $I(\omega)$ using harmonic bath for the environment. Ref., Chap. 21.1-21.6; Z, Chap. 3; Ro, Chap. 1; LL, Sec 123; D, Chap. 2; K, Chap. 2-2.2; Han, Chap. 7.1-7.2; Ha, Chap. 6.1.

6. *Fokker-Planck and Related Equations*: Stationary process; Markov process, stationary; Ornstein-Uhlenbeck process; nonstationary Markov process; Wiener-Levy process; Chapman-Kolmogorov equation; Fokker-Planck equation for probability density of velocities; Smoluchowski equation; Fokker-Planck equation for distribution of velocity and space coordinates; Applications: free diffusion, molecule in a uniform field, damped oscillator; Kramers equation and chemical reactions and limiting cases and transition state theory; Deduction of Smoluchowski equation from the more general F.-P. equation; Molecular basis of the Langevin equation. Ref. Chap. 20; F, Chaps. 11-13; vk, Chap. 8; P, Chap. 10; D, Chap. 12; Re, Chap. 6G; K, Chap. 2.3-2.4; Han, Chap. 7.3; Ha, Chap. 4.3, 6.3-6.6; Ri, Chaps. 4.4-4.8, 5.1-5.5; Z, Chaps 2 and 4.

7. *Linear response theory:* Statistical mechanical treatment of linear response; Response to an alternating electric field, frequency dependent conductivity $\sigma(\omega)$; Second fluctuation-dissipation theorem (random force autocorrelation); Response to electric field [$\sigma(\omega)$], and use of linear response formalism; Comments on fluctuation-dissipation theorem for hydrodynamic coefficients; Static structure factor; Dynamic structure factor; inelastic neutron scattering; Use of Kramers-Konig relations. Ref., Chaps. 21.7-21.9; F, Chap. 14; Re, Chap. 15 H; LL, Sect. 123-125; K, Chaps. 3-3.2, 4-4.2; D, Chaps. 1, 3; Han, Chap. 7.5-7.8; Ri, Chap. 7; L, Chap. 1.4-1.5; Z, Chap. 7.

8. *References*: "Ref" is an abbreviation for D. A. McQuarrie, *Statistical Mechanics* (Harper, 1976), the principal text for the class. The other references are C.V. Heer, *Statistical Mechanics, Kinetic Theory and Stochastic Processes* (Academic, 1972) (**He**); N.G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, 1983) (**vK**); L.E. Reichl, *A Modern Course in Statistical Physics* (U. Texas Press, 1980) (**Re**); L.D. Landau and E. M. Lifschitz, *Statistical Physics* (Vol. 5 of "Theoretical Physics"), 3rd ed. (Pergamon, 1980) (**LL**); H. L. Friedman, *A Course in Statistical Mechanics*, (Prentice-Hall, 1985) (**F**); K. Huang, *Statistical Mechanics* (Wiley 1987), 2nd ed. (**Hu**); R. Kubo, M. Toda and N. Hashitsume, *Statistical Physics. II. Nonequilibrium Statistical Mechanics*, 2nd Ed. (Springer, 1991) (**K**); H. Risken, *The Fokker-Planck Equation* (Springer, 1984) (**Ri**); J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids, 2nd Ed.* (Academic, 1986) (**Han**); H. Haken, *Synergetics, An Introduction to Nonequilibruim Phase Transitions and Self-organization in Physics, Chemistry, and Biology* (Springer, 1983) (**Ha**); S. W. Lovesey, *Condensed Matter Physics: Dynamic Correlations* (**L**); L. Waldmann, Chap. in *Handbuch der Physik*, vol. XII, ed. by S. Flugge (Berlin) (in Ger.) (**W**); W. G. Rothschild, *Dynamics of Molecular Liquids* (Wiley, 1984) (**Ro**); J. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes* (Springer, 1987) (**K**); S. Dattagupta, *Relaxation Phenomena in Condensed Matter Physics* (Academic, 1987), (**D**); H. L. Pecseli, *Fluctuations in Physical Systems* (Cambridge U. P. 2000) (**P**); R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford Univ. Press, 2001) (**Z**). **Z** in Chaps. 8 and

9 contains useful topics (projection operators, nonlinear problems) not considered in the outline #1-7.

Books

A new book, *Nonequilibrium Statistical Physics,* by N. Pottier (Oxford Univ. Press, 2010) looks very interesting, and also brings in the topic of the thermodynamics of irreversible processes. It is on statistical physics (e.g., thermoelectric effect, thermal diffusion, Lorentz gas, etc.) rather than being primarily on chemical physics applications. There is nevertheless much overlap with material in the current course.

The books reserved in the library for this course are:

- Statistical Mechanics by D. A. McQuarrie (Harper, 1976), QC 178.M23;
- A Course in Statistical Mechanics by H. L. Friedman, (Prentiss Hall, 1985), QC 174.8, F75;
- Statistical Physics II. Nonequilibrium Statistical Mechanics, 2nd Edition by R. Kubo, M. Toda. N. Hashimume (Springer, 1991) QC 174.8 T613; and
- Nonequilibrium Statistical Physics by N. Pottier (Oxford University Press, 2010), QC174.86.N65 P68 2010.