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 $\phi = 1\text{n} f$; *H*-theorem; Steady-state (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; Role 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 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*(ω) 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 σ(ω); Second fluctuation-dissipation theorem (random force autocorrelation); Response to electric field [σ(ω)], 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.

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.

Lecture Topics Summary
Nonequilibrium Statistical Mechanics
Tues. & Thurs. 9:00 – 10:25 a.m.
Chem. 166, Rm. 147 Noyes

Lecture 1

Early history of 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
Boltzmann equation

Lecture 2

Collisions. Center of mass and laboratory system of coordinates. Classical mechanics of collisions.
Differential scattering cross section.
Scattering angle versus impact parameter
Rainbow angle
Inverse Collisions
Collision term in the Boltzmann equation

Lecture 3

Boltzmann transport equation
H-theorem, steady-state
Collisional invariants
Comments on systematic solution of the Boltzmann integro-differential equation for the single particle distribution function
Expressions for fluxes (energy, momentum)
Transport coefficients: perturbative approximation to obtain the single particle distribution. Use of orthogonal polynomials for heat conductivity, viscosity and others.

Lecture 4

Boltzmann equation for electrical conductivity in a solid. Solution of equation. Einstein relation between mobility and diffusion coefficient.
Relation between diffusion coefficient and integral of velocity autocorrelation function
Discrete random walk. Mean square velocity change of colloidal particle. Stokes Law, and Einstein expression for the diffusion constant
Langevin equation, particle under random and frictional forces
Solution of Langevin equation for a random variable v: fluctuations of v and mean square deviation of v from its mean at time t ; Gaussian random variable: deduction of the probability distribution $P(v, t \mid v_o,0)$ from these results

Lecture 5

Probability distribution $P(x, t \mid x_o.0)$ deduced from the solution of $x(t)$, mean and mean square deviation of $x(t)$, and Gaussian random variable property of $x(t)$

Expression for $\langle (x - x_o)^2 \rangle$, when the average is over displacement and then over the initial velocity

Brownian Motion. History. Difference of Einstein (1905) and Ornstein-Uhlenbeck (1930) results. Earlier "paradox" at small t.

Estimate of ζ. Dependence of Brownian motion on particle size, viscosity, and temperature of particle.

Lecture 6

Langevin equation, overdamped harmonic oscillator, mean square displacement

Velocity autocorrelation function (C_{VV}(t)) of free particleand diffusion, from solution of the Langevin equation. First fluctuation-dissipation theorem.

Fourier-Laplace transform of C_{VV}(t)

Convolution theorem

Generalized Langevin equation (GLE). A particular model for the memory function $M(t)$

Lecture 7

Interlude: Complex variables: Cauchy Residue theorem,

Fourier-Laplace transform solution.

Generalized Langevin equation (GLE), solution (completed)

Other examples of $M(t)$

Mori-Zwanzig basis for GLE

Langevin equation for harmonic oscillator with inertia and damping

Lecture 8

Relation of correlation function to spectral density, Wiener-Khinchin theorem

Application ot W-K theorem to harmonic oscillator with inertia and damping.

Microscopic reversibility and relation between correlation functions $\langle A(0)B(t)\rangle$ and $\langle B(0)A(t)\rangle$. Examples

Assigned as problem: Second fluctuation dissipation theorem (fluctuations of random force)

Lecture 9

Memory function and correlation function, time scales.

Memory function. Determination from computations.

Infrared absorption and Lorentzian

Characteristic function and moments

Energy loss of damped harmonic oscillator in liquids

Lecture 10

Relation of Langevin equation for several variables to the generalized Langevin equation (GLE) for fewer variables, harmonic oscillator as an example

Cumulant expansion and truncation to two-time point correlation (Kubo)

Golden Rule. Optical absorption. Correlation function for transition dipole moment.

Role of modulation rate and magnitude in determining shape of optical absorption band (yielding Gaussian and Lorentzian as limits)

Lecture 11

Role of modulation rate (cont'd)
Example of expression for $I(\omega)$ using harmonic bath for the environment
Noise, $1/f$, white and other

Lecture 12

$1/f^2$ noise (Brownian noise)
Markov process.
Example of stationary Markov process: Ornstein-Uhlenbeck process for velocity in Brownian motion
Examples of nonstationary Markov processes: Wiener-Levy process for position in Brownian motion; Poisson process for probability of number of events in t.
Calculation of moments and test for stationarity of a random process

Lecture 13

Chapman-Kolmogorov equation
Fokker-Planck equation for distribution of velocities
Evaluation of $<(\Delta v)>$ and $<(\Delta v)^2>$ for use in F. P. equation
Smoluchowski equation for distribution of coordinates and application to diffusion

Lecture 14

Smoluchowski equation and application to sedimentation, damped oscillator, and chemical reaction rates

Lecture 15

Smoluchowski equation and chemical reaction rates (cont'd), including transition state and internal diffusion limits
F.-P. equation in phase space: distribution of velocity and space coordinates
Deduction of Smoluchowski equation from the more general F.-P. equation (Kramers) and also by perturbation method, analogous to that used for Boltzmann equation
Example of the extended Langevin equation. Frequency-dependent conductivity $\sigma(\omega)$ and its relation to the auto-correlation function of the current density
Remark: A topic not given in lectures (problem set 5): Use of harmonic analysis for linear stochastic equations (Langevin equation)

Lecture 16

Linear response theory, response function $\phi_{BA}(t)$
Linear response theory, treatment based on regression of fluctuations from a nonequilibrium state, relation of response function to a correlation function
Response to an oscillating force, dynamic susceptibility $\chi_{BA}(\omega)$
Work done under time-varying force. Two related approaches: work done on system, work done on force
Relation of dissipation to the imaginary part of complex susceptibility; Fluctuation-dissipation theorem
Application of linear response theory to infrared absorption spectra,

conductivity, and (Prob.Set 7) dielectric polarization

Outlined in an instructional handout: Relation between power spectrum and auto-correlation function of a stochastic variable (Wiener-Khinchin Theorem)

Lecture 17

Liouville equation for time-dependent distribution function and statistical mechanics of linear response theory. $<A(0)\ B(t)> = (A(-t)\ B(0)>$

Linear perturbation of distribution function and resulting expression for response function