Chemistry 448
Tentative Course outline

1. Introduction
2. Some definitions and assorted mathematical methods
   distributions, occupation numbers, distribution function
   permutations, configurations, system quantum states
   boltzon bosons fermions
   ensemble average, the most probable distribution
   Lagrange multipliers, Stirling's approximation
3. Statistical mechanics of a system of one kind of particles, non-interacting
   the molecular partition function
   the nature of alpha and beta
   interpretation of heat and work
   interpretation of entropy
4. Atoms and diatomic molecules
   energy levels and partition functions
   distribution laws and thermodynamic functions
   nuclear spin statistics
5. Classical statistical mechanics
   classical phase space
   equipartition of energy
6. Polyatomic molecules
   symmetry number, vibrations
   classical partition functions with and without internal rotation
7. Statistical mechanics and chemical equilibrium
8. Canonical and grand canonical ensembles
   thermodynamic functions
   systems with more than one component
9. Fluctuations
   density fluctuations in the grand ensemble
   the random walk
   diffusion and the random walk
10. Systems of interacting particles
    canonical partition function
    distribution functions, pair correlation functions
    the assumption of pair potentials
    second virial coefficient of hard spheres
    the Lennard-Jones fluid
    ensemble averages of dynamical variables and molecular properties
    more about intermolecular potentials
    phase transformations
11. Computer simulations (open-ended and actually starts in earlier sections)

Chemistry 448
Reading List, in alphabetical order by author

There is no textbook for the course. Instead we have a reading list and for each topic, a part of one or more books will be very helpful, in addition to the lecture notes. Some are old textbooks, but are still good and easy to read. Others are on computer simulations. In some books on the list we will use only one or two chapters. The same topic is treated in different ways by different authors, so you can look around to find what suits you best to supplement the lectures. Since the class is small, I have checked out of the library some books which I will be responsible for, and which we will have for the use of the entire class until April 30, 2001. These are marked with the symbol ☑. I also have my personal copies on the list, and these are marked ☒. These books will be available in Room 4240 SES.

The other (unmarked) books on the list (as well as those marked ☒) are available in the Science Library. You may wish to check them out yourself for your own use.

If you wish to do computer simulations for your research, you will need to own the first book on the list.

☒ M. P. Allen and D. J. Tildesley, Computer Simulation of Liquids, Clarendon Press, Oxford

☑. Frank Andrews, Equilibrium Statistical Mechanics, John Wiley

☑. Radu Balescu, Equilibrium and Non-equilibrium Statistical Mechanics, John Wiley

☑. K. Binder, ed. The Monte Carlo Method in Condensed Matter Physics, Springer-Verlag

☑. K. Binder, ed. Applications of the Monte Carlo Method in Statistical Physics, 2nd edition, Springer-Verlag

☑. K. Binder and D. W. Heermann, Monte Carlo Methods in Statistical Physics, An Introduction, 3rd edition, Springer

☑. Roger Bowley and Mariana Sanchez, Introductory Statistical Mechanics, Clarendon Press, Oxford

☒ David Chandler, Introduction to Modern Statistical Thermodynamics, Oxford University Press

Norman R. Davidson, Statistical Mechanics, John Wiley

Malcolm Dole, Introduction to Statistical Thermodynamics (an easy-to-read primer)

Richard P. Feynman, Statistical Mechanics: a Set of Lectures

☑. E. S. R. Gopal, Statistical Mechanics and Properties of Matter, Theory and Applications, John Wiley

☒ Dieter W. Heermann, Computer Simulation Methods in Theoretical Physics, Springer-Verlag

   Terrell L. Hill, Statistical Mechanics: Principles and Selected Applications QC175.H49 (he wrote more than one book)

☑. E. Atlee Jackson, Equilibrium Statistical Mechanics, Prentice-Hall

   McQuarrie, Statistical Thermodynamics

☑. George D. J. Phillies, Elementary Lectures in Statistical Mechanics, Springer

1. INTRODUCTION

I. INTRODUCTION

STATISTICAL MECHANICS — the application of the laws of mechanics (quantum and classical) to the microscopic motions of atoms and molecules in order to DERIVE all the pertinent MACROscopic laws:

  laws of thermodynamics
  chemical kinetics
  fluid dynamics
  dielectric phenomena
  magnetic phenomena
  elasticity

In other words, statistical mechanics provides the molecular foundation of the above.

THE QUESTION:

If particles (atoms, molecules, or electrons and nuclei, ...) obey certain microscopic laws with specified interparticle interactions, what are the observable properties of a system containing a very large number of such particles?

In other words, we want to discuss the relationship between the microscopic dynamics or fluctuations (as governed by Schrödinger's equation or Newton's laws of motion) and the observed properties of a large system (such as the heat capacity or equation of state)

Why use a statistical approach?

N = number of particles $\sim 10^{23}$

microscopic: Do we need to evaluate directly the precise N-particle dynamics? To reproduce the precise time evolution of a many-body system, one must specify at some initial time a macroscopic number of variables $(\sim 10^{23})$ such as initial coordinates and momenta of all particles if they are *classical* or an equally cumbersome list of numbers if they are quantal. If we fail to list just one of these $\sim 10^{23}$ variables, the time evolution of the system would no longer be deterministic and an observation that depended on the precise time evolution would no longer be reproducible.

MACROSCOPIC: At thermodynamic equilibrium one can characterize observations of a macroscopic system with ONLY A HANDFUL OF VARIABLES. It is possible to reproduce a physical system in many different laboratories by specifying a small number of other macroscopic properties. There are distinctive regularities in the behavior of macroscopic bodies.

Assume: STATISTICAL LAWS governing the behavior of systems composed of very many particles lead to these regularities and Probability Statistics provides the correct description of what we see during a macroscopic measurement.

If an observable of a many-particle system can be specified by a small number of other macroscopic properties, we assume that the observable can be described with STATISTICAL MECHANICS

trajectory – the time evolution of a system

- A quantal system obeying Schrödinger's eqn

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \mathcal{H} |\Psi\rangle$$

Consider the stationary solutions of N non-interacting particles in a box

$$\mathcal{H} |\Psi_\nu\rangle = E_\nu |\Psi_\nu\rangle$$

ν is the collection of $D \cdot N$ quantum numbers where D = dimensionality
Once the initial state is specified, if it could be, the state at all future times is determined by the time integration of Schrödinger's eqn.

- A classical system obeying Newton's eqn of motion

$$\frac{d\vec{p}}{dt} = \vec{F}$$

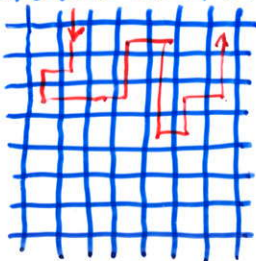The initial point in phase space
$$(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots \vec{r}_N; \vec{P}_1, \vec{P}_2, \vec{P}_3 \cdots \vec{P}_N)$$
characterizes completely the microscopic state of a classical system. The time evolution of the system of N particles is determined by the time integration of Newton's eqn of motion.

Now think about this time evolution – the trajectory of a many-body system with, for example, N, V, and E fixed.

trajectory
in state space
(phase space or
Hilbert space)

each box
represents
a different
state

Basic concept in statistical mechanics:
IF WE WAIT LONG ENOUGH, THE SYSTEM WILL
EVENTUALLY FLOW THROUGH ALL THE MICROSCOPIC
STATES CONSISTENT WITH THE IMPOSED CONSTRAINTS.

That is, after a long enough time, all states are
visited.

If a measurement of a property is made over
the long time we get the <u>time average</u> of
the property G

$$G_{obs} = \frac{1}{M} \sum_{a=1}^{M} G_a$$

during the ath measurement whose time duration is so short that the system is in only one microscopic state

rewrite

$$= \sum_{\nu} \left[\frac{1}{M} * \left(\begin{array}{l} \text{number of times} \\ \text{state } \nu \text{ is observed} \\ \text{in the M observations} \end{array} \right) \right] G_{\nu}$$

$$\langle \nu | G | \nu \rangle$$

expectation value in state ν

$$G_{obs} = \sum_{\nu} P_{\nu} G_{\nu} = \langle G \rangle$$

probability of finding system in state ν

$\langle G \rangle$ ensemble average

<u>time average</u>   =   ensemble average

is believed to hold for all many-body systems
encountered in nature (<u>ergodic systems</u>)

Ergodic systems sample all possible states
after a very long time.

Primary assumption of statistical mechanics:
The observed value of a property corresponds
to the ENSEMBLE AVERAGE of that property.

OR else,

consider even a short time measurement
but imagine the observed macroscopic
system to be divided into an assembly
of many macroscopic subsystems still large
enough. When the molecular behavior
in one subsystem is uncorrelated with that
in any of the neighboring subsystems, then
one INSTANTANEOUS MEASUREMENT of the total
macroscopic system is equivalent to many
independent measurements of the subsystems.
The many independent measurements should
correspond to an ENSEMBLE AVERAGE