

# Time-Dependent Statistical Mechanics

## 1. Introduction

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Lecture

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### Announcements

## 1 Topics of concern in the course

We shall be concerned with the time dependent behavior of macroscopic systems that are at or near thermodynamic equilibrium. The time dependence of interest is that involved with the mechanism by which the system approaches equilibrium and the ways in which properties of an equilibrium system fluctuate in time.

### Properties of interest

- Transport coefficients
  - diffusion constants
  - thermal conductivity coefficients
  - viscosity coefficients
- Relaxation rates
  - spin-lattice relaxation and dephasing times
  - rotational relaxation times
  - rate constants for chemical reactions

- Spectroscopic properties and scattering properties
  - Absorption spectrum (electromagnetic radiation)
  - Scattering cross sections (light, neutrons, x-rays)
  - Other spectroscopic experiments (e.g. echoes)

These properties have a number of things in common.

- They are typically measured for systems that are at equilibrium or close to equilibrium.
- There are close physical and mathematical relationships among this class of properties.
- Time- and/or space-dependent correlation functions provide a useful language for describing each of these.

### Model systems

- Atomic or molecular fluid with complete classical description of interactions and motion (molecular dynamics calculations)
- Particles suspended in a continuum fluid (e.g. colloids, Brownian particles, polymer dissolved in a solvent)
- Dilute gas of molecules suffering random collisions
- Molecular degrees of freedom coupled to a thermal bath (e.g. nuclear spins and two-level systems)
- Ising spin systems and lattice gases

A wide variety of model systems are used in physical chemistry.

- Some are essentially microscopic; some use a mixture of microscopic and macroscopic ideas.
- Some have a large number of variables; some have a small number.
- Some are realistic; some are very schematic.

An interesting thing about these models is that often we use different models for the same system. For example, a polymer solution might be described as a large molecule dissolved in a molecular fluid. Or it might be described as a set of beads

connected by springs and suspended in a continuum solvent. Each of the models that is used presumably has some region of validity. Understanding the relationship between various models used for the same system is very important for the proper use of a theory.

### **Ways of describing the dynamics of a physical/chemical system**

- Deterministic mechanics
  - Classical mechanics
  - Quantum mechanics
- Stochastic dynamics
  - Monte Carlo dynamics
  - Langevin dynamics
  - Smoluchowski dynamics
  - Random walk models
  - Collision models
- Hydrodynamic, transport, or rate equations
  - Navier-Stokes equations
  - Diffusion equations
  - Chemical rate equations

A wide variety of dynamical descriptions are used in physical chemistry.

- Some are essentially microscopic; some are macroscopic; some are a mixture of both types of ideas.
- Some are classical and some are quantum.
- Some are deterministic and some are stochastic.

As is the case for model systems, it is often the case that different dynamical descriptions are used for the same system. Each of the dynamical descriptions presumably has some region of validity. Understanding the relationship between the different dynamical descriptions is very important for the proper use of the theory.

In treating any particular problem of interest, one must in general choose a combination of an appropriate model system and an appropriate dynamical description that will work on that model. Or one might choose several such combinations for the same system of interest. In this course, we shall not be able to discuss all the possible combinations, but we shall discuss some specific combinations and discuss some of the underlying theory in enough depth that you will be able to begin to understand the variety of ways in which this class of time dependent problems is approached in physical chemistry and so that you will be able to have a somewhat unified picture of the relationships among these theoretical ideas.

## 2 Unifying ideas for the problems of interest for the course

**Ensemble postulate of statistical mechanics** provides the overall framework for the use of probability and statistics in discussing mechanical systems

### The hierarchy of dynamical descriptions

- Classical or quantum mechanics on an atomic and molecular level, taking all the molecules into account, is the most fundamental description. It is valid on a molecular time and distance scale.
- Intermediate descriptions, e.g.
  - random walk models
  - Brownian motion
  - Monte Carlo dynamics

These are valid on longer time scales and (usually) longer distance scales.

- Hydrodynamic (macroscopic) equations are the description appropriate for the longest time scales and distance scales.

### The interrelationships among the various levels in the hierarchy

- Each description is valid (if at all) on its specific time and length scales and presumably longer time and length scales as well but not on shorter time and distance scales.
- With the exception of the hydrodynamic equations, each becomes more intractable and less useful when you try to apply them on a time or length scale that is longer than the one for which it was originally devised.
- Each description, if it is valid, is in principle derivable from the most microscopic one. In practice, however, the derivation may not have been constructed yet. Thus the use of any particular dynamical description for any particular system is essentially a hypothesis (a guess) that this will work.
- Often there are consistency conditions that can be derived by demanding that different descriptions be consistent with one another. These consistency conditions can be very useful, and understanding how to use them is often very important in development of an appropriate theory.

**Time and space dependent correlation functions** provide a unifying description of many experimentally observable quantities as well as many quantities that are important in the development of the theory. These functions appear when transport, scattering, and relaxation analyzed using linear response theory and certain formulations of scattering theory. A correlation function is an average of a product of two properties.

- The density autocorrelation function<sup>1</sup> of a liquid,  $\langle \rho(\mathbf{R}, t)\rho(\mathbf{R}', t) \rangle$ , describes the correlation between the density of molecules or atoms at two different positions at the same time. This is related to the way the material scatters x-rays. The density autocorrelation function is typically as close as we can come to measuring or understanding the structure of a liquid.
- The same autocorrelation function for different values of the time arguments,  $\langle \rho(\mathbf{R}, t)\rho(\mathbf{R}', t') \rangle$ , describes the correlation between the density of molecules or atoms at two different positions at two different times. This is related to the way the material scatters light or neutrons.

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<sup>1</sup>Here the angular brackets denote an average over an equilibrium ensemble. We shall discuss the precise meaning of this pretty soon. For the moment, you can regard this as some sort of average for an equilibrium system.

- The velocity autocorrelation function  $\langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(t') \rangle$  describes the correlation between the velocity of a molecule at one time and the velocity of the same particle at a different time. The self-diffusion coefficient of the molecule can be calculated from the velocity autocorrelation function.
- The dipole autocorrelation function  $\langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t') \rangle$  describes the correlation between the electric dipole moment vector of a molecule at one time and the electric dipole vector of the molecule at a different time. The dielectric relaxation spectrum of a material is related to this correlation function. The dipole moment vector of a molecule is related to the orientation of the molecule.

In a liquid, the molecules are constantly translating and rotating. The diffusion coefficient in effect tells us something about the translational motion of the molecules, and the dielectric constant in effect tells us something about the rotational motion of the molecules.

I hope that by the end of the course you will have developed the following habit. Whenever you are trying to understand any experimental technique that measures a *rate* or a *spectrum* or a *transport coefficient*, you automatically ask yourself “What correlation function does this quantity measure?” . If you ask this question, you are on your way to a meaningful understanding of the experiment and to an understanding of how that experiment is related to other types of measurements.

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