Lecture 1
CHE 210C: Topics in Nonequilibrium Statistical Mechanics

1. Introduction and Classical Mechanics Primer

A. Course Objectives

In this course, we hope to accomplish several things:

1. Provide an intro to non-equilibrium classical (non-quantum) systems
2. Develop insights into the molecular origins of macroscopic transport phenomena
3. Develop tools for studying time-dependent phenomena in gases, liquids, complex fluids

As a means of introducing the course and illustrating item 2, let us now consider a simple example of tracer diffusion:
B. A Tracer Diffusion Example

Consider a dilute gas of a monatomic substance A (e.g., argon), into which we inject a single atom of a labeled (isotope) A, denoted A*. We inject the atom at the origin and with initial momentum $P_0$.

We now ask:

1. How does the tracer particle equilibrate with the surrounding gas?

2. How is diffusive transport of the tracer achieved at larger length scales and time scales?
First, we address question 1. We know from our studies of equilibrium that, at equilibrium, the momenta of the various atoms in a fluid are uncorrelated (independent) and distributed according to the Maxwell–Boltzmann PDF:

\[ f_M(p) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{p^2}{2m k_B T}} \]

where \( p^2 = p_x^2 + p_y^2 + p_z^2 \)

\[ \beta = \frac{1}{k_B T} \]

The average squared momentum of a particle is

\[ \langle p^2 \rangle = \int dp \ f_M(p) \ p^2 = 3m k_B T \]

and a "typical" momentum is

\[ p_{rms} = \sqrt{\langle p^2 \rangle} = \sqrt{3m k_B T} \]

Now, how does a particle injected with some \( p_0 \) achieve the "typical" momentum? Clearly, by collisions...
with the other atoms, or the walls. Let's assume the system is big, and ignore the wall collisions. Let the typical distance that an atom travels between collisions be denoted \( \lambda \). This is the mean free path. As an atom moves a distance \( \lambda \), it sweeps out a volume \( \lambda \pi (d/2)^2 \), such that any other atom within that volume will suffer a collision with it:

![Diagram](image)

If the atoms interact (like hard spheres), then \( d \) is the atomic diameter. More typically, \( d \) is of order the range of the interatomic potential \( \langle v(r) \rangle \).

The mean free path is defined as the distance \( \lambda = \lambda \) such that
the volume swept out contains exactly one other atom, implying one collision. Thus

\[ \lambda = \frac{1}{\pi d^2 \rho} \]

where \( \rho = N/V \), the average number density of the gas, can be used to estimate \( \lambda \), i.e.

\[ \lambda \approx \frac{1}{\pi d^2 \rho} \]

*Note that in estimating \( \lambda \), we neglect precise spatial & temporal correlations between pairs of particles, e.g. the density of other particles is estimated as \( \rho \). This is a type of mean-field approximation.

Given an estimate of the distance an atom travels between collisions, we can estimate the time between collisions as

\[ \tau \approx \frac{1}{\langle r_{\text{travel}} \rangle} \approx \frac{1}{\pi d^2 \rho \left( \frac{m}{3 k_B T} \right)^{1/2}} \]

"collision time"

\( \tau \approx 10^{-12} \text{ sec in liquid Argon and is reduced as } \tau \approx \rho^{-1} \text{ as the density is lowered in a gas. Obviously} \)
the estimate is more reliable in the limit of a very dilute gas, where collisions are infrequent and pairwise.

We can now address the first question in our tracer experiment: the tracer particle will adjust its momentum from $p_0$ to a typical value $P_{\text{rms}}$ after a few collisions, by energy and momentum exchange with the surrounding particles. Hence

$$t_{\text{equil}} = \Theta(\tau) \approx 5 \tau$$

Next, let's study how the average position of the tracer atom spreads out due to collision events with other atoms:
Consider a microscopic tracer concentrat,
\[ C_m(x, t) = \delta [x - \xi(t)] \]
where \( \xi(t) \) is the position of the tracer at time \( t \). We can think of \( C_m(x, t) \, dx \) as the probability of observing the tracer in volume \( dx \) at time \( t \), at least after averaging over all trajectories \( \xi(t) \).

Note the normalization,
\[ \int dx \, C_m(x, t) = 1 \]

If \( n = \frac{t}{\tau} \) collisions occur over \( (0, t) \) and the tracer moves force-free between collisions, we can write,
\[ \xi(t) = \int_0^t \tilde{v}(s) \, ds + t \sum_{j=1}^{n} \frac{\mathbf{p}_j}{m} \]

where the \( \mathbf{p}_j \), \( j = 1, 2, \ldots, n \) are random momenta, selected from the MB distribution. We can then affect
the "trajectory average" by the following

\[ C(t, t) = \langle C_n (x, t) \rangle \]

\[ = \prod_{j=1}^{n} \left[ \int dp_j \, f(p_j) \right] S \left[ x - \frac{\vec{p}_j}{m} \right] \]

These \( n \) integrals do not factor because of the \( S \) line. However, if we Fourier transform:

\[ C(k, t) = \int dx \, e^{ik \cdot x} C(x, t) \]

\[ C(k, t) = \prod_{j=1}^{n} \left[ \int dp_j \, f(p_j) e^{i \frac{\vec{p}_j}{m} \cdot \vec{k}} \right] \]

\[ = \left[ \int dp f(p) e^{i \frac{\vec{p}}{m} \cdot \vec{k}} \right]^n \]

\[ = \left[ e^{-\frac{1}{2m} \vec{k} \cdot \vec{k} \cdot T} \right]^n \]

To derive this last expression, you need the Gaussian integral formula:

\[ \int dp_x e^{-a \vec{p}^2 / 2 + b \vec{p} \cdot \vec{x}} = \left( \frac{2\pi a}{2} \right)^{n/2} e^{-b \cdot \vec{x} / a} \]
Finally, with \( nT = t \):

\[
C(k, t) = e^{-Dk^2t}
\]

Here \( D \) is a self-diffusion coeff:

\[
D = \frac{k_B T \tau}{2m} \sim \left(\frac{k_B T}{m}\right)\frac{1}{d}\rho^{-1} \sim \lambda\frac{\text{Pms}}{m}
\]

This is our first example of deriving a transport coefficient from microscopic principles. How did we know to identify \( D \) as a diffusion coeff? Suppose \( C(x, t) \) spreads diffusively at long times:

\[
\frac{\partial}{\partial t} C = D \nabla^2 C, \quad C(x, 0) = \delta(x)
\]

Fourier transforming:

\[
\frac{\partial}{\partial t} C(k, t) = -Dk^2 C(k, t)
\]

\[
C(k, 0) = 1
\]

\[
C(k, t) = e^{-Dk^2t}
\]
Let's now summarize what we have accomplished.

a. Made molecular-based estimates of $\lambda$, $\tau$, and $D$ in a dilute gas.

b. Shown that collisions lead to diffusive transport behavior for $t \gg \tau$.

c. Argued that collisions are responsible for momentum equilibration in a fluid.

Obviously, we arrived at the above results for a dilute gas by invoking several physically-motivated approximations. We now turn to a more rigorous approach that will provide the foundations for an exposition of the principles of non-equilibrium Statistical Mechanics.
2. Classical Statistical Mechanics

A. Formulations of Classical Mechanics for Many-Particle Systems

In this course our focus will be on classical fluid systems of key interest to chemical engineers and "soft materials" scientists. We begin with the simplest system, a monatomic fluid, and set up a system relevant to $SN$ calculations in the Canonical Ensemble.

The degree of freedom of the system in classical mechanics correspond to the $3N$ particle positions $\mathbf{x}^N = (\mathbf{x}_1, \ldots , \mathbf{x}_N)$ and the $3N$ particle momenta: $\mathbf{p}^N = (p_x, \ldots , p_z)$.