This course builds on the elementary concepts of statistical mechanics that were introduced in ChE 210A and provides a more in-depth exploration of topics related to simple and complex fluid systems at equilibrium. ChE 210C introduces non-equilibrium statistical mechanics.

* Discuss course info sheet / office hrs / web site
* Discuss syllabus

Let’s now launch into our introductory lecture, reviewing the basic principles of equilibrium statistical mechanics:

1. Introduction and Review of Equilibrium Statistical Mechanics

A. Classical fluid systems of interest

As chemical engineers or “complex fluids” oriented materials scientists, you will repeatedly encounter a variety of fluid systems of varying complexity, e.g.,

- Atomic liquids (1 Å): e.g. condensed noble gases A, Xe, ...
- Diatomic liquids (2-3 Å): e.g. O₂, CO, N₂, ...
- Molecular liquids (2-5 Å): e.g. H₂O, CO₂, CH₄, ...
- Polymers (50-500 Å): e.g. polyethylene, polystyrene, ...
- Colloids (0.1-10 µm): e.g. latex particles, clays, ...

All of these systems can be described quite accurately at thermodynamic equilibrium by using the principles of classical (as opposed to quantum) statistical mechanics. We shall primarily focus on such systems and on the condensed
liquid state, rather than the gas state (which you have already treated in ChE 210A) and the solid state (which is treated in courses on solid state physics). Note the “coarse-graining” of our “cartoons” as we move up in lengthscale.

B. Averages and Ensembles

Let us now review the way in which averages are computed in statistical mechanics. Suppose that within a large volume of a gas or liquid, you had a smaller “measurement volume” in which you could count the number of particles. Imagine that you made a large number $M$ of such measurements over a long time period and the system was at equilibrium. Then, you could compute the “time average” of the number of particles $N$ inside the permeable barrier by

$$\bar{N} = \lim_{M \to \infty} \frac{1}{M} \sum_{i=1}^{M} N_i$$

where $N_i$ is the number of particles in $i$th observation.

We shall see later in the course that such time averages, constructed by following a particular dynamical trajectory of one system, are the most convenient way calculating equilibrium averages in computer simulations. It is of course also what we do in experimental measurements on fluids!

There is another convenient way of averaging in statistical mechanics. A basic tenant of statistical mechanics is that after a long enough time, all microscopic states $\nu$ (quantum or classical) in a given system will be visited. Thus, we should also be able to construct an “ensemble average”

$$\langle N \rangle = \sum_{\nu} P_{\nu} N_{\nu}$$

where $P_{\nu}$ is the probability of the $\nu$th microstate occurring and $N_{\nu}$ is the number of particles inside the barrier in this microstate. This is called an ensemble average because the right hand side can be constructed by making
one measurement on a large number ("ensemble") of identical equilibrium system at the same time, weighting the observation of a particular microstate by its frequency of occurrence.

The **ergodic hypothesis** of statistical mechanics says that

\[ \bar{N} = \langle N \rangle \]

This is generally met in most systems that you will encounter in your scientific or engineering careers. However, there are notable exceptions—e.g., glasses. Generally, systems are **ergodic** when there is largely unrestricted flow and access to the various microstates throughout their dynamical trajectories. This "flow" is often closely associated with the trajectories becoming chaotic due to nonlinearities in the dynamical equations. Thus, it turns out that there is a close connection between statistical mechanics (a relatively old subject) and one of the “hottest” areas of contemporary theoretical research: nonlinear dynamics.

Different ensembles are convenient for calculations in statistical mechanics, depending on what constraints are imposed on a system. To mimic an isolated system that cannot exchange energy or mass with its surroundings, we use the

**C. Microcanonical Ensemble** \((N, V, E)\)

To begin we define a quantity known as the microcanonical partition function:

\[ \Omega(N, V, E) = \text{number of states with } N, V, \text{ and energy } E \text{ fixed} \]

Next, we invoke a fundamental postulate of statistical mechanics that **all states of the same energy are equally likely at equilibrium**. In other words, these states are characterized by a uniform probability distribution, \(P_\nu\). It follows that

\[ P_\nu = \begin{cases} \frac{1}{\Omega(N, V, E)} & \nu \in \text{states of ensemble} \\ 0 & \nu \notin \text{states of ensemble} \end{cases} \]

Using this distribution function, we can compute ensemble averages of some property \(G\):

\[ \langle G \rangle = \sum_\nu P_\nu G_\nu \]

where \(G_\nu\) is the value of \(G\) in microstate \(\nu\). The connection to thermodynamics is via **Boltzmann's formula** for the entropy:

\[ S = k_B \ln \Omega(N, V, E) \]

We shall see that in each ensemble there is such a connection between a thermodynamic quantity (in this case the entropy \(S\)), referred to as a “thermodynamical potential”, and the logarithm of a partition function (in this case \(\Omega\)).
We can now use standard thermodynamics relations to get all the other equilibrium properties. Recall that the internal energy $E$ in an isolated system satisfies

$$dE = dq - dw = T dS - p dV \quad \text{"1st Law"}$$

closed system

$$T = \left( \frac{\partial E}{\partial S} \right)_{V,N} \quad \text{or} \quad \beta \equiv \frac{1}{k_B T} = k_B^{-1} \left( \frac{\partial S}{\partial E} \right)_{V,N}$$

$$\beta = \left( \frac{\partial \ln \Omega}{\partial E} \right)_{V,N}$$

gives temperature

$$p = T \left( \frac{\partial S}{\partial V} \right)_{E,N} = \beta^{-1} \left( \frac{\partial \ln \Omega}{\partial V} \right)_{E,N}$$

gives pressure

D. The Canonical Ensemble ($N, V, T$)

This is another very important ensemble. Here we consider systems closed to mass transfer, but open to energy flow and in contact with a heat bath at temperature $T$.

In this ensemble, different states can have different internal energies and the probability of occurrence of a state $\nu$ of energy $E_\nu$ is now not uniform, but “Boltzmann-distributed”:

$$P_\nu = \frac{e^{-\beta E_\nu}}{Q(N, V, T)} = \frac{e^{-\beta E_\nu}}{\sum \nu e^{-\beta E_\nu}} \quad \text{"canonical partition function"}$$

Again, notice that $T$, rather than $E$, is constant and $E_\nu$ varies with state $\nu$ in the ensemble. Also, $P_\nu$ is evidently normalized such that $\sum_\nu P_\nu = 1$. Thus, $\langle G \rangle = \sum_\nu P_\nu G_\nu$ gives the ensemble average of a quantity $G$ as before.
Now, let’s make the thermodynamics connections. The average internal energy should be:

\[ E = \langle E \rangle = \sum_{\nu} E_{\nu} e^{-\beta E_{\nu}} / Q \]

\[ = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = \left( -\frac{\partial \ln Q(N,V,T)}{\partial \beta} \right)_{N,V} \]

But, recall that the Helmholtz free energy is defined by

\[ A(N,V,T) = E - TS \]

\[ dA = dE - TdS - SdT \]

\[ S = -\frac{\partial A}{\partial T} \] \text{V,N}

Thus,

\[ E = A + TS = A - T \left( \frac{\partial A}{\partial T} \right)_{V,N} = k_B T \frac{\partial \ln Q}{\partial T} \]

Notice that the last two expressions can be viewed as a 1st order, inhomogenous, linear ordinary differential equation for \( A \) as a function of \( T \) at fixed \( V \) and \( N \). A particular solution is

\[ A(N,V,T) = -k_B T \ln Q(N,V,T) \]

which represents the fundamental connection to thermodynamics in the canonical ensemble. In this important ensemble \( A \) is thermodynamic potential that is logarithmically related to the canonical partition function \( Q \). Notice that there is also a homogeneous solution \( \text{const} \times T \) to the differential equation, but the constant coefficient must vanish or the third law of thermodynamics would be violated (vanishing entropy of a perfect crystal at \( T = 0 \)).

The pressure can be computed in the canonical ensemble according to

\[ P = -\frac{\partial A}{\partial V} \] \text{N,T}

\[ = k_B T \frac{\partial \ln Q}{\partial V} \] \text{N,T}

and similar expressions can be used to calculate all other thermodynamic quantities.

Finally, we return to the entropy expression

\[ S = -\frac{\partial A}{\partial T} \] \text{V,N}

Let’s show that this is equivalent to the Gibbs entropy formula

\[ S = -k_B \sum_{\nu} P_{\nu} \ln P_{\nu} \]
which holds for any ensemble. The manipulations are as follows:

\[
P_\nu \ln P_\nu = Q^{-1} e^{-\beta E_\nu} [-\beta E_\nu - \ln Q] \\
\sum_\nu P_\nu \ln P_\nu = -\beta \langle E \rangle - Q^{-1} (\ln Q) Q \\
-k_B \sum_\nu P_\nu \ln P_\nu = \frac{1}{T} \langle E \rangle + k_B \ln Q \\
\quad = \frac{E - A}{T} \equiv S
\]

There are many other ensembles that one can choose besides the microcanonical and canonical. For example, it is natural in many experiments to maintain control over the variables \( P, T, N \). The \((P, T, N)\) ensemble is referred to as the “isothermal-isobaric” ensemble and you will have opportunity to work with it in your homework exercises. We now turn to consider the most important other one: the grand canonical ensemble.

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**Lecture 2**

Reading: 3.6–3.7, 7.1 Chandler, Chapter 3 McQuarrie

Recap: ergodic hypothesis

ensembles, \( \beta \equiv k_B T \)

<table>
<thead>
<tr>
<th>ensemble</th>
<th>part. func</th>
<th>thermo connection</th>
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<tbody>
<tr>
<td>micro. can. (NVE)</td>
<td>( \Omega(N,V,E) = \sum_\nu )</td>
<td>( S = k_B T \ln \Omega )</td>
</tr>
<tr>
<td>canonical (NVT)</td>
<td>( Q(N,V,T) = \sum_\nu e^{-\beta E_\nu} )</td>
<td>( A = -k_B T \ln Q )</td>
</tr>
<tr>
<td>grand can. ((\mu VT))</td>
<td>( Q_G(\mu,V,T) = \sum_\nu e^{-\beta (E_\nu - \mu N_\nu)} )</td>
<td>( pV = k_B T \ln Q_G )</td>
</tr>
<tr>
<td></td>
<td>( S = -k_B \sum_\nu P_\nu \ln P_\nu )</td>
<td>Gibbs entropy formula</td>
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**E. The Grand Canonical Ensemble \((\mu,V,T)\)**

In the grand canonical ensemble we consider a system open to both mass transfer and energy flow. This can be most easily realized if our system is part of a larger system with a mass and energy permeable boundary separating the two.
Thus, $N$ and $E$ both fluctuate from state to state. We control the $N$ fluctuations by imposing a chemical potential $\mu$. Recall from the thermodynamics of open systems
\[
dE = TdS - pdV + \mu dN
\]
\[
dA = -SdT - pdV + \mu dN,
\]
that $\mu$ is the conjugate thermodynamic variable to $N$. Indeed, $(T, S)$, $(p, V)$, and $(\mu, N)$ are all conjugate pairs.

One might guess that the appropriate distribution is thus
\[
P_\nu = e^{-\beta (E_\nu - \mu N_\nu)} / Q_G
\]
where
\[
Q_G(T, V, \mu) = \sum_\nu e^{-\beta (E_\nu - \mu N_\nu)}
\]
is the “grand partition function”, which is usually given the symbol $\Xi$ (but I hate to draw this on the board!). Indeed, one can prove that this is the distribution that maximizes the Gibbs entropy formula $S = -k_B \sum_\nu P_\nu \ln P_\nu$ subject to the following constraints:

1. $\sum_\nu P_\nu = 1$
2. $\sum_\nu E_\nu P_\nu = \langle E \rangle$
3. $\sum_\nu N_\nu P_\nu = \langle N \rangle$

You may also want to review the material in Chapter 1 of McQuarrie on the method of Lagrange multipliers. With this choice of $P_\nu$, the Gibbs formula gives
\[
S = -k_B \sum_\nu P_\nu [-\beta E_\nu + \beta \mu N_\nu - \ln Q_G]
\]
\[
= + \frac{1}{T} \langle E \rangle - \frac{\mu}{T} \langle N \rangle + k_B \ln Q_G
\]
or
\[
k_B T \ln Q_G = TS - E + \mu N
\]

Now, recall the following definition of the Gibbs free energy:
\[
G = A + pV = E - TS + pV
\]
However, $G$ is an extensive function that can be expressed in terms of its “partial molar” property $\mu$.
\[
G = \mu N = N \frac{\partial G}{\partial N}_{T,p}
\]
Thus,
\[
k_B T \ln Q_G = TS - E + G
\]
or
\[
[pV = k_B T \ln Q_G(T, V, \mu),]
\]
which serves as the fundamental connection to thermodynamics in the grand canonical ensemble. The combination \( pV \) plays the role of the thermodynamic potential in this ensemble.

The average energy is

\[
E \equiv \langle E \rangle = \sum_\nu E_\nu P_\nu = Q_G^{-1} \sum_\nu E_\nu e^{-\beta E_\nu + \beta \mu N_\nu}
\]

Thus,

\[
-Q_G^{-1} \frac{\partial}{\partial \beta} Q_G \rangle_{\mu,V} = \langle E \rangle - \mu \langle N \rangle
\]

Similarly

\[
N = \sum_\nu N_\nu P_\nu = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Q_G \rangle_{T,V}
\]

**F. Fluctuations**

It is important to appreciate that the variables that are not held fixed will fluctuate in the various ensembles. We can often relate these fluctuations to higher-order derivatives of the thermodynamic potentials. Such formulas are particularly useful in computer simulations. As an example, consider energy fluctuations in the canonical ensemble:

\[
\delta E \equiv E - \langle E \rangle \quad \langle (\delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle
\]

\[
= \langle E^2 \rangle - 2\langle E \langle E \rangle \rangle + \langle \langle E \rangle^2 \rangle
\]

\[
= \langle E^2 \rangle - \langle E \rangle^2
\]

\[
= \sum_\nu E_\nu^2 P_\nu - (\sum_\nu E_\nu P_\nu)^2
\]

\[
= \frac{1}{Q} \frac{\partial^2}{\partial \mu^2} \ln Q - \left( -\frac{1}{Q} \frac{\partial}{\partial \beta} Q \right)^2
\]

\[
= \frac{\partial^2}{\partial \beta^2} \ln Q \rangle_{N,V}
\]

\[
= -\frac{\partial}{\partial \beta} \langle E \rangle
\]

Now, recall that

\[
C_v = \left( \frac{\partial E}{\partial T} \right)_{N,V}
\]

const. \( V \) heat capacity

\[
\frac{\partial}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \Rightarrow
\]

\[
-k_B T^2 C_v = \left( \frac{\partial E}{\partial \beta} \right)_{N,V} = -\langle (\delta E)^2 \rangle
\]
Thus, in the canonical ensemble, we can calculate the heat capacity via

\[ C_v = \frac{1}{k_B T^2} \langle (\delta E)^2 \rangle \]

This is referred to as a “fluctuation formula” for the heat capacity. From the expression on the right hand side, we might naïvely think that \( \langle (\delta E)^2 \rangle \sim N^2 \), as one increases the size of a system. However, \( C_v \) is extensive (recall that \( C_v = \frac{3}{2} N k_B \) for a structureless ideal gas), so

\[ \langle (\delta E)^2 \rangle \sim N \text{ or } \langle (\delta E)^2 \rangle^{1/2} \sim N^{1/2} \]

Alternatively,

\[ \frac{\langle (\delta E)^2 \rangle^{1/2}}{\langle E \rangle} \sim \frac{N^{1/2}}{N} \sim \frac{1}{N^{1/2}} \longrightarrow 0 \]

as \( N \rightarrow \infty \). Thus, the fluctuations become vanishingly small for systems of macroscopic size, \( N \sim 10^{23} \).