Lecture 18

Objectives:

1. Be able to describe how intermolecular potentials give rise to nonideal fluid and solid behavior.
2. Be able to discuss the origin of intermolecular forces.
3. Be able to give examples of several model interaction potentials and discuss their advantages and limitations.
4. Be able to derive the Helmholtz free energy residual function from statistical mechanics.

1. Semi-classical partition function:

\[ Q = \frac{Z_{\text{int}}}{N!A^N} \]

\[ Z = \int \cdots \int \exp \left[ -\beta U(q^N) \right] dq^N \]

Note that \( Z \) contains all the intermolecular interactions. Note that \( Z \) is the only density dependent part of the factored semi-classical partition function. \( Q_{\text{int}} = Q_{\text{ideal gas}} \).

2. Origin of Fluid Nonidealities

The configurational partition function \( Z \) contains all the density dependent information, hence all the fluid nonidealities are contained in \( Z \). If we could evaluate \( Z \) for a real fluid then we would have the problem solved.

3. Evaluation of \( U \)

The total potential energy is a function of the positions (not momenta) of all the molecules in the system.

\[ U = U(q^N) \]

but we can rigorously written as an infinite sum of two-body, three-body, etc. potentials.

\[ U = \sum_{i<j} u(q_i, q_j) + \sum_{i<j<k} \Delta u_{ijk}(q_i, q_j, q_k) + \ldots \]

where \( u_{ij} = u(q_i, q_j) \) is the potential between two isolated molecules. \( \Delta u_{ijk} \) is the term that accounts for distortions of the pair potential due to the presence of the third molecule, etc. You can see that the higher terms should go to zero rather quickly. We often assume that three body and higher potentials are zero, i.e.,

\[ U = \sum_{i<j} u_{ij} \]

4. What forces give rise to \( U \)?

The potential between an isolated pair of molecules is due to the interactions among the nuclei and electrons on each molecule. These are very complex and are the subject of quantum mechanics. However, we can qualitatively understand the potential in terms of classical Coulombic interactions.
(a) **Electrostatic.** Present if the molecule is charged, e.g., hydroxide (OH\(^-\))

(b) **Polar.** Present in most molecules to some extent, but not in atoms. This depends on symmetry, but a classic example is water, as the electrons on the hydrogens have a relatively higher probability of being close to the oxygen atom.

(c) **Induction or Dispersion.** These are present in all molecules and atoms. This has to do with the electron correlation effect and is quantum mechanical in nature.

(d) **Overlap.** Present in all molecules and atoms. When two molecules get close enough their electron clouds will start to repel each other, causing a very sharp increase in potential energy.

(e) **Association.** Hydrogen bonding in water, this is somewhere in between induction and chemical bond formation. Present in only a few types of molecules. Water is the best example (hydrogen bonding). Charge transfer is another example.

5. **Model Potentials**

Let us assume that pair-wise additivity is accurate. Quantum mechanics says that the repulsive potential can be modeled by

\[ u_{ij}^{\text{rep}} = Be^{-br} \]

and the attractive or dispersion forces can be modeled as an infinite series

\[ u_{ij}^{\text{disp}} = - \left[ \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} + \ldots \right] \]

where each of the coefficients must be identified for a specific type of molecule. We assume that the molecule is spherically symmetric in such a treatment, but not really because we can define an angle averaged potential that is a function of temperature that is rigorous.

Empirical potential models have been developed. Some of them are listed here.

(a) **Hard Sphere Potential.**

\[ u(r) = \begin{cases} \infty & \text{for } r < \sigma \\ 0 & \text{for } r > \sigma \end{cases} \]

(b) **Square Well Potential.**

\[ u(r) = \begin{cases} \infty & \text{for } r < \sigma \\ -\epsilon & \text{for } \sigma < r < \lambda \sigma \\ 0 & \text{for } r > \lambda \sigma \end{cases} \]

(c) **Sutherland Potential.**

\[ u(r) = \begin{cases} \infty & \text{for } r < \sigma \\ -\epsilon \left( \frac{\sigma}{r} \right)^6 & \text{for } r > \sigma \end{cases} \]

(d) **Lennard-Jones Potential.**

\[ u = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]
There are many more potentials, but this gives you an idea about the main features. The Lennard-Jones potential is perhaps the most used in statistical mechanics. Maybe a tie with the hard sphere potential.

The force on a pair of molecules in 3-d from the Lennard-Jones potential is

$$\vec{F}_{ij} = -\vec{\nabla} u(r_{ij})$$

where

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$


We have an EOS for the ideal gas, which we have seen we can derive from statistical mechanics. The configurational partition function contains the potential of the system, which is responsible for departures from ideal gas behavior. We could write our departure functions in terms of the partition function.

$$A^{\text{ideal gas}}(N, V, T) - A(N, V, T) = -kT \ln \frac{Q}{Q^{\text{ideal gas}}}$$

$$\Delta A'(N, V, T) = kT \ln \left[ \frac{Z Q_{\text{int}}^{N A^3}}{V^N Q_{\text{int}}^{N A^3}} \right] = kT \ln \frac{Z}{VN}$$

What is the relationship between the pair potential and the equation of state for the real fluid? Recall that

$$\Delta J'(T, p) = \Delta J'(T, N, V) + \int_V^{nRT/p} \left( \frac{\partial J'}{\partial V} \right)_T dV$$

Then

$$\Delta A'(T, p) = A^{\text{ideal gas}}(N, V, T) - A(N, V, T) + \int_V^{nRT/p} \left( \frac{\partial A'}{\partial V} \right)_T dV$$

But,

$$\int_V^{nRT/p} \left( \frac{\partial A'}{\partial V} \right)_T dV = -NkT \int_V^{nRT/p} \left( \frac{\partial \ln V}{\partial V} \right)_{T,N} dV = -NkT \ln (\frac{nRT}{pV}) = NkT \ln z$$

$$\Delta A'(T, p) = kT \ln \frac{Z}{VN} + NkT \ln z$$

Recall that

$$\Delta J'(T, p) = \int_V^{\infty} \left[ \left( \frac{\partial J'}{\partial V} \right)_T - \left( \frac{\partial J}{\partial V} \right)_T \right] dV + \int_V^{nRT/p} \left( \frac{\partial J'}{\partial V} \right)_T dV$$

Therefore,

$$\Delta A'(T, p) = \int_V^{\infty} \left[ p - \frac{nRT}{V} \right] dV + nRT \ln z.$$
In molecular terms,

\[ kT \ln \frac{Z}{VN} = \int_{\infty}^{V} \left[ p - \frac{NkT}{V} \right] dV \]

Therefore,

\[ \Delta p' = \left( \frac{\partial \Delta A'}{\partial V} \right)_{T,N} = -kT \left( \frac{\partial \ln \frac{Z}{VN}}{\partial V} \right)_{T,N} = \frac{NkT}{V} - kT \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N} \]