Lecture 1 - AMM Course

Main Topics

- Thermodynamics + Statistical Mechanics
- Monte Carlo methods for statistical sampling
- Molecular Dynamics
- Analysing simulation data
- Advanced methods

Supplementary Reading

- Understanding Molecular Simulation - Daan Frenkel & Berend Smit
- Statistical Physics of Particles - Mehran Kardar
- Introduction to Modern Statistical Mechanics - David Chandler

Objectives of Materials Modelling

1. Understand / rationalising experimental observations.
2. Materials discovery / predicting material design / optimisation properties at different length + time scales.

- Atomistic description to understand Macroscopic behaviour.
- Thermodynamic stability
- Mechanical properties
- Phase transitions
- Nanoscale structure

Hierarchy of Materials Modelling

- **QM (Quantum Mechanics):** Schrödinger / Dirac exact / rigorous.
- **Atomistic:** Approximate (but systematically improvable).
- **Meso Scale**
- **Continuum:** Includes phenomenological, logical models.

    The **Partition Function** is a useful tool for connecting atomistic Degrees of Freedom (DOF) (micro) to Thermodynamic observables (macro).

Brief overview of thermodynamics

A phenomenological description of macroscopic systems in thermal equilibrium.

Zeroth Law

This describes the transitive nature of equilibrium (it came after the I, II, & III laws).

If 2 systems A & B are separately in equilibrium with a third system, C, then they are in equilibrium with one another. (Maxwell: "All heat is of the same kind").

Thermodynamic Variables

These are functions purely of the TD (thermodynamic) state of a system, not of its history / preparation / microstates.

- **Intensive variables** (don't depend on system size):

  - pressure, p

  - temperature, T

  - chemical potential, μ

- **Thermodynamic Potentials:**

  - internal energy, U

  - enthalpy, $H = U + pV$

  - Helmholtz free energy, $F = U - TS$

  - Gibbs free energy, $G = U - TS + pV$

  - Grand potential, $\Phi = U - TS - \mu N$

First law of thermodynamics

The work required to change a state of a system depends only on the initial and final states, not on the means by which the work is performed, nor the path taken. This is a conservation law.

Note: Thermodynamic potentials cannot always be determined in absolute values, only up to a constant shift.

Differential Forms & Maxwell Relations

- **Internal energy, U:**
  $$dU = \delta W + \delta Q = -pdV + TdS$$
  From this, we can derive:
  $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $p = -\left(\frac{\partial U}{\partial V}\right)_S$
  (but how to fix entropy in the lab?)

- **Enthalpy, H:**
  $$H = U + pV$$
  $$dH = dU + V\,dp + p\,dV = T\,dS + V\,dp$$

- **Helmholtz free energy, F:**
  $$F = U - TS$$
  $$dF = -SdT - pdV$$
  From this, we get a more useful definition of pressure, as Temperature (T) can be controlled:
  $p = -\left(\frac{\partial F}{\partial V}\right)_T$

- **Gibbs free energy, G:**

$$G = U - TS - pV$$
$$dG = -SdT + V\,dp$$

Summary

Thermodynamics is the foundation to obtain macroscopic properties.