From Atoms to Materials: Predictive Theory and Simulations

Week 4: Connecting Atomic Processes to the Macroscopic World
Lecture 4.1: Statistical Mechanics: Connecting the Micro and Macro Worlds

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Relate microscopic phenomena and macroscopic properties

• Given a series of microscopic states, what is the corresponding macroscopic state?
• Given a thermodynamic state of a material, what are the probabilities of finding the system in the various possible microscopic states?
Microscopic probabilities: isolated systems

Consider $N$ atoms in a rigid container of volume $V$ with constant energy $E$

What is the probability of finding the state in a given microscopic state?

$$\{ R_i \} \quad \{ P_i \}$$

A simple case: 1-D harmonic oscillator:

$$H = \frac{P^2}{2m} + \frac{1}{2} KX^2$$

$$\Delta x \Delta p \geq \hbar$$

Number of states with energy $E$:

$$\Omega(E) = \frac{1}{\hbar} \int dX \int dP \delta(E - H(X, P))$$
Equal a-priori probabilities

Consider $N$ atoms in a rigid container of volume $V$ with constant energy $E$

In general: number of different possible microscopic states:

$$\Omega(E,V,N) = \frac{1}{N! h^{3N}} \int d^3R \int_{-\infty}^{\infty} d^3P \delta\left(H\left(\{R_i\},\{P_i\} - E\right)\right)$$

**Postulate**: the probability of the material being in any one of the $\Omega(N,V,E)$ is the same, i.e. all states are equally likely

$$P(\{R_i\},\{P_i\}) = \begin{cases} \frac{1}{\Omega(E,V,N)} & \text{if } H(\{R_i\},\{P_i\}) = E \\ 0 & \text{otherwise} \end{cases}$$
• Consider a fictitious separation that divides the material in two subsystems

• Energy can be exchanged between subsystems 1 and 2

What is the probability of subsystem 1 having energy $E_1$?

$$P(E_1, E - E_1) = \frac{\text{Number of microstates with } E_1 \text{ in sub-sys 1}}{\Omega(E, V, N)}$$

$$P(E_1, E - E_1) = \frac{\Omega_1(E_1, V_1, N_1) \cdot \Omega_2(E_2, V_2, N_2)}{\Omega(E, V, N)}$$

Additive measure of number of states:

$$\log P(E_1, E - E_1) = \log \Omega_1(E_1, V_1, N_1) + \log \Omega_2(E - E_1, V - V_1, N - N_1) + C$$
Statistical mechanics

- Equilibrium state of the material:
  - Subsystems have the most likely energies: maximum of \( \log P(E_1, E - E_2) \)

\[
\frac{\partial \log P(E_1, E - E_1)}{\partial E_1} = 0 = \frac{\partial \log \Omega_1(E_1, V_1, N_1)}{\partial E_1} + \frac{\partial \log \Omega_2(E - E_1, V - V_1, N - N_1)}{\partial E_1}
\]

Since \( E_2 = E - E_1 \):

\[
\frac{\partial}{\partial E_1} = - \frac{\partial}{\partial E_2}
\]

In equilibrium:

\[
\frac{\partial \log \Omega_1(N_1, V_1, E_1)}{\partial E_1} = \frac{\partial \log \Omega_2(N_1, V_1, E_1)}{\partial E_2}
\]

\[
\beta(E, V, N) = \frac{\partial \log \Omega(E, V, N)}{\partial E}
\]

\[
\beta_1(E_1, V_1, N_1) = \beta_2(E_2, V_2, N_2)
\]
Stat Mech: microcanonical ensemble

$log \Omega$ is important enough to have its own name: entropy

$$S = k \log \Omega(E, V, N)$$

Temperature:

$$\frac{\partial S(E, V, N)}{\partial E} = \frac{1}{T}$$

$$\frac{\partial \Omega(E, V, N)}{\partial E} = \beta = \frac{1}{kT}$$

Pressure:

$$\frac{\partial S(E, V, N)}{\partial V} = -\frac{P}{T}$$

Chemical potential:

$$\frac{\partial S(E, V, N)}{\partial N} = \frac{\mu}{T}$$
Statistical mechanics: further reading

• Kerson Huang: “Statistical Mechanics”

• Landau and Lifshitz: “Course of Theoretical Physics Volume 5: Statistical Physics”

• Balescu: “Equilibrium and nonequilibrium statistical mechanics”