6. Statistical Mechanics

Outline

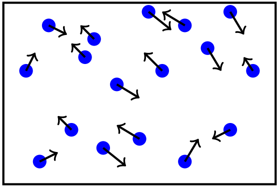
Statistical mechanics

- a mathematical framework that applies *statistical methods* and *probability theory* to large assemblies of microscopic entities
- studies physical *systems* that consist of a large number of entities, such as atoms, molecules, or others
- aims to explain the *macroscopic properties* of the system without having to solve the *detailed dynamics* of all the entities
- provides a *bridge* between the *microscopic world* and the *macroscopic world*

Important concepts

- *system* - the collection of entities under consideration
- *environment* - everything outside the system
- *microstate* - the complete specification of the state of the system.
  - in quantum mechanics, a microstate is a quantum state of the system, characterized by a wave function
  - in classical mechanics, a microstate is the complete specification of the positions and velocities of all the entities
  - will use the quantum mechanical definition of microstate until otherwise stated
- the i-th microstate of the system is denoted by $|i\rangle$

An example system



- the system consists of a large number of gas molecules
- in quantum mechanics, a microstate is a quantum state of the system specified by a wave function
- in classical mechanics, a microstate is the complete specification of the positions and velocities of all the molecules, i.e., a vector of $6N$ numbers where N is the number of molecules

Postulates of statistical mechanics

- a system with fixed number of particles N, volume V, and energy E is equally likely to be found in any of its microstates
- over a long time period, the system spends equal amount of time in each of its microstates

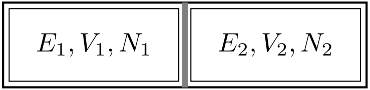
Outline

Entropy

- $\Omega(E, V, N)$ - the number of microstates of the system with energy E, volume V, and number of particles N
- entropy S of the system is defined as

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

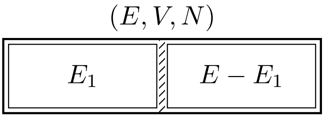
  where k_B is the Boltzmann constant
- when two subsystems are combined with no interactions into one system



  - $\Omega_{\text{total}} = \Omega_1 \cdot \Omega_2$
  - $S_{\text{total}} = S_1 + S_2$

Temperature

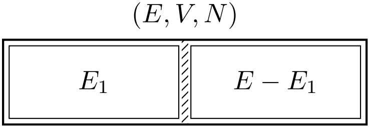
- when two subsystems are combined and allowed to exchange energy



- E_1 is the energy of the first subsystem and varies among the microstates of the system
- $\Omega(E_1, E - E_1)$ - the number of microstates of the system when the first subsystem has energy E_1 and the second subsystem has energy $E - E_1$
- $\Omega(E_1, E - E_1) = \Omega_1(E_1) \cdot \Omega_2(E - E_1)$
- $\ln \Omega(E_1, E - E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E - E_1)$

Temperature

- when two subsystems are combined and allowed to exchange energy



- what is the most probable value of E_1

- each microstate is equally likely, so the most probable value of E_1 is the one that maximizes $\Omega(E_1, E - E_1)$, or equivalently, maximizes $\ln \Omega(E_1, E - E_1)$

$$\left(\frac{\partial \ln \Omega(E_1, E - E_1)}{\partial E_1} \right)_{N,V,E} = 0$$

Temperature

- find the most probable value of E_1 by maximizing $\ln\Omega(E_1, E-E_1)$

$$\left(\frac{\partial \ln\Omega(E_1, E-E_1)}{\partial E_1}\right)_{N,V,E}$$

$$= \left(\frac{\partial \ln\Omega_1(E_1)}{\partial E_1}\right)_{N_1,V_1} + \left(\frac{\partial \ln\Omega_2(E-E_1)}{\partial E_1}\right)_{N_2,V_2}$$

$$= \left(\frac{\partial \ln\Omega_1(E_1)}{\partial E_1}\right)_{N_1,V_1} - \left(\frac{\partial \ln\Omega_2(E_2)}{\partial E_2}\right)_{N_2,V_2} = 0$$

- the most probable value of E_1 is the one that satisfies

$$\left(\frac{\partial \ln\Omega_1(E_1)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial \ln\Omega_2(E_2)}{\partial E_2}\right)_{N_2,V_2}$$

Temperature

- for a system with energy E, volume V, and number of particles N,

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

- two systems are in thermal equilibrium if

$$\beta_1(E_1, V_1, N_1) = \beta_2(E_2, V_2, N_2)$$

- the temperature of a system is defined as

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

- $\beta = 1/(k_B T)$

Outline

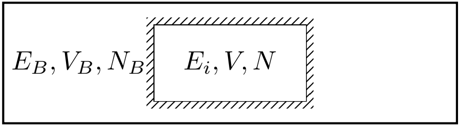
Postulate

Entropy and temperature

Boltzmann distribution

A system in thermal equilibrium with a heat bath

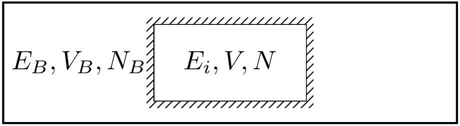
- the total system consists of the system and a heat bath



- E_i - the energy of the system when it is in microstate i
- E_B - the energy of the heat bath
- the total energy $E = E_i + E_B$ is conserved
- what is the probability P_i that the system is in microstate i

Boltzmann distribution

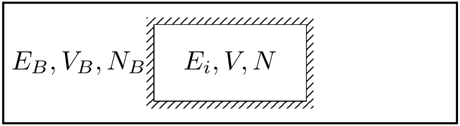
- P_i - the probability that the system is in microstate i



- the microstate of the total system is specified by the microstate of the system and the microstate of the heat bath
- when the system is in microstate i, the heat bath can be in any of its microstates with energy $E_B = E - E_i$
- P_i is proportional to the number of microstates of the heat bath with energy $E_B = E - E_i$ because the total system is equally likely to be in any of its microstates

Boltzmann distribution

- P_i - the probability that the system is in microstate i



- $P_i \propto \Omega_B(E - E_i)$

- P_i needs to be normalized so that $\sum_i P_i = 1$

$$P_i = \frac{\Omega_B(E - E_i)}{\sum_j \Omega_B(E - E_j)}$$

Boltzmann distribution

- P_i - the probability that the system is in microstate i

$$P_i = \frac{\Omega_B(E - E_i)}{\sum_j \Omega_B(E - E_j)}$$

- to compute $\Omega_B(E - E_i)$, expand $\ln \Omega_B(E - E_i)$ around $E_i = 0$

$$\ln \Omega_B(E - E_i) = \ln \Omega_B(E) - E_i \cdot \frac{\partial \ln \Omega_B(E)}{\partial E} + \cdots$$

- the Boltzmann distribution

$$P_i = \frac{\exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)} = \frac{\exp(-E_i/k_B T)}{\sum_j \exp(-E_j/k_B T)}$$

  where T is the temperature of the heat bath

- after reaching thermal equilibrium, the system has temperature T

Partition function

- for a system with fixed N, V, T, its *partition function* is defined as

$$Q = \sum_j \exp(-\beta E_j)$$

- the probability that the system is in microstate i is

$$P_i = \frac{\exp(-\beta E_i)}{Q}$$

- the average energy of the system is

$$\langle E \rangle = \sum_i E_i P_i = \frac{\sum_i E_i \exp(-\beta E_i)}{Q} = -\frac{\partial \ln Q}{\partial \beta}$$

- the Helmholtz free energy of the system is

$$F = -k_B T \ln Q$$

Observables

- in quantum mechanics, an observable A is represented by an operator and its value when the system is in microstate i is $\langle A \rangle_i = \langle i | A | i \rangle$
- the average value of the observable A is

$$\langle A \rangle = \frac{\sum_i \exp(-E_i/k_B T) \langle i | A | i \rangle}{\sum_j \exp(-E_j/k_B T)}$$

Classical statistical mechanics

- in classical mechanics, the microstate of the system is specified by the positions and momenta of all the particles $\{\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots\}$
- the *phase space* of the system is the space of all possible microstates
- given a microstate, the energy of the system consists of a kinetic energy term and a potential energy term

$$E(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots) = K(\mathbf{p}_1, \mathbf{p}_2, \ldots) + U(\mathbf{r}_1, \mathbf{r}_2, \ldots)$$

- the *probability density* of the system in phase space is

$$\rho(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots) = \frac{\exp(-\beta E)}{Q}$$

- the partition function is defined as

$$Q = \int \exp(-\beta E)\, d\mathbf{r}_1\, d\mathbf{p}_1\, d\mathbf{r}_2\, d\mathbf{p}_2\, \ldots$$

Classical statistical mechanics

- because $E(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots) = K(\mathbf{p}_1, \mathbf{p}_2, \ldots) + U(\mathbf{r}_1, \mathbf{r}_2, \ldots)$ is a sum of two terms that depend on $\{\mathbf{r}_1, \mathbf{r_2}, \ldots\}$ and $\{\mathbf{p}_1, \mathbf{p_2}, \ldots\}$ separately, the probability density can be written as

$$\rho(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots) = \rho_{\text{pos}}(\mathbf{r}_1, \mathbf{r}_2, \ldots) \cdot \rho_{\text{mom}}(\mathbf{p}_1, \mathbf{p}_2, \ldots),$$

where

$$\rho_{\text{pos}}(\mathbf{r}_1, \mathbf{r}_2, \ldots) = \frac{\exp(-\beta U)}{Q_{\text{pos}}}; \; \rho_{\text{mom}}(\mathbf{p}_1, \mathbf{p}_2, \ldots) = \frac{\exp(-\beta K)}{Q_{\text{mom}}}$$

- the partition function can be written as $Q = Q_{\text{pos}} \cdot Q_{\text{mom}}$ where

$$Q_{\text{pos}} = \int \exp(-\beta U)\, d\mathbf{r}_1\, d\mathbf{r}_2\, \ldots$$

$$Q_{\text{mom}} = \int \exp(-\beta K)\, d\mathbf{p}_1\, d\mathbf{p}_2\, \ldots$$

Classical statistical mechanics

- in many cases, we are mostly interested in the positions of the particles and not their momenta
- the Boltzmann distribution on the positions of the particles is

$$P(\mathbf{r}_1, \mathbf{r}_2, \ldots) = \frac{\exp(-\beta U(\mathbf{r}_1, \mathbf{r}_2, \ldots))}{Q_{\mathsf{pos}}},$$

  where $Q_{\mathsf{pos}} = \int \exp(-\beta U)\, d\mathbf{r}_1\, d\mathbf{r}_2\, \ldots$

- the average value of an observable A is

$$\langle A \rangle = \frac{\int \exp(-\beta U) A(\mathbf{r}_1, \mathbf{r}_2, \ldots)\, d\mathbf{r}_1\, d\mathbf{r}_2\, \ldots}{\int \exp(-\beta U)\, d\mathbf{r}_1\, d\mathbf{r}_2\, \ldots}$$