

# Statistical Mechanics

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## Basics and Terminology

- For a discrete random variable  $X$ , the average or *expected value* of  $X$  is given by  $\langle X \rangle := \sum_i X_i P_i$  where  $X_i$  are the possible values of  $X$  and  $P_i$  are the probabilities of those values.
- For a continuous variable  $x$  with PDF  $P(x)$ , the expected value is  $\mathbb{E}[x] := \int x P(x) dx$ .
- *Entropy* is a measure of how much information has been lost.
  - For a discrete variable  $X_i$  with probabilities  $P_i$ , entropy is given by  $S := -\sum_i P_i \log(P_i)$ .
  - For a continuous variable  $x$  with PDF  $P(x)$ , entropy is given by  $S := -\int P(x) \log P(x) dx$ .
  - The basic unit of entropy is  $\log(2)$  and is called a *bit*.
  - If the exact state of a variable  $X$  is known with 100% certainty, then the entropy is always 0, and if nothing is known then the entropy is maximized.
  - For physical systems, the entropy is often thought of as being parameterized by the energy with higher energy configurations having greater entropies.
- The *temperature* of a system is defined by  $T := \frac{\partial E}{\partial S}$ .
- The *Boltzmann constant*  $\kappa_B$  is a conversion factor between human units (such as temperature) and laboratory units. It varies depending on the actual units, but is usually proportional to  $\kappa_B \approx 10^{-23} \frac{\text{Joules}}{\text{Kelvins}}$ .
- The fluctuation of a system given by the deviation from the mean value, and is computed  $\sigma^2 := \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$ .

Statistical mechanics is an alternative to classical mechanics used when the initial conditions, laws of motion, and outside forces of a system cannot be known with 100% accuracy.

Consider a system whose initial condition is known to be contained in a blob  $B$  in phase space with volume  $V_B$ . Then Liouville's theorem states that after any finite amount of time, if we could track the trajectories of all the particles in  $B$  exactly, they would be located in a new blob of phase space  $B^*$  with volume  $V_B$ . In this scenario, the number of phase points  $(x, p)$  and their corresponding probabilities would be preserved (though they would correspond to new locations), so the entropy would remain constant. As seen here, perfect preservation of information corresponds to stationary entropy, while in general, entropy tends to increase as information is lost over time.

## The Laws of Thermodynamics

**The First Law:** The First Law of Thermodynamics states that for a closed system, energy is a conserved quantity:  $\frac{dE}{dt} = 0$ . More generally,  $dE = -PdV + TdS$  where  $E$  is energy,  $P$  is pressure,  $T$  is temperature  $V$  is volume, and  $S$  is entropy. Then the function  $Q$  defined by  $dQ := TdS$  is called the heat function and the function  $W$  defined by  $dW := PdV$  is called the work function. Clearly, for a closed system there is no time dependence so  $\frac{dE}{dt} = 0$ , but it is also interesting to note that  $W$  and  $Q$  are not well-defined functions since  $dQ$  and  $dW$  are not generally conservative.

**The Second Law:** The Second Law of Thermodynamics states that entropy always increases. This is because of the fact that information is always lost, since every computation is inexact. These errors compound, until we are maximally uncertain of the state of the system. This does **not** imply that a system can never return to its initial conditions. In fact, the chaotic nature of most systems ensures that after a finite amount of time the system will come arbitrarily close to any configuration in phase space. In particular, it can and will return arbitrarily close to its initial conditions in the future. The time it takes (on average) for a system to return to some initial state is called the *Poincaré recurrence*, and is proportional to  $e^{S_0 - S_t}$  where  $S_0$  is the entropy of the initial state and  $S_t$  is the total entropy of the system.

**The Zeroth Law:** For two systems  $A$  and  $B$  that are allowed to share energy, the first law tells us that  $\dot{E}_A + \dot{E}_B = 0$ , and the second law tells us that  $\dot{S}_A + \dot{S}_B > 0$ . Also, recall that  $T = \frac{\partial E}{\partial S}$ . These equations are enough to show that if  $T_A > T_B$ , then energy will flow from system  $A$  into system  $B$  until  $T_A = T_B$ , a state called *thermal equilibrium*.

## The Boltzmann Distribution

Consider the question of what distribution of states we should expect to see in a meta system composed of several identical subsystems that share energy. Let the states of the subsystems be given by  $X_i$ , with energy  $E_i$  and entropy  $S_i$ . The problem of maximizing the number of ways to achieve a certain distribution such that the total energy is conserved is equivalent to the problem of maximizing the entropy. The *Boltzmann distribution* is the probability distribution  $P_i$  over the states  $X_i$  that maximizes the entropy of the system. In the discrete case, it is given by  $P_i := \frac{1}{z} e^{-\beta E_i}$  where  $z := \sum_i e^{-\beta E_i}$  is called the *partition function*, and  $\beta := \frac{1}{T}$  is the inverse temperature. In the continuous case, it is identical except  $z \rightarrow \int e^{-\beta E(x)} dx$ .

So, in summary, the distribution of states for a set of interacting subsystems is typically given by the Boltzmann distribution (of maximum entropy). Furthermore, note that the Boltzmann distribution favors states of low energy over states of high energy, meaning most of the states will have low energy. The state of lowest energy is called the *ground state*. Given the Boltzmann distribution, the expected energy and entropy of any individual subsystem are given by

$$\langle E \rangle = -\frac{\partial \log z}{\partial \beta} \quad \text{and} \quad \langle S \rangle = \beta E + \log z.$$

## Ideal Gas and the N-Body Problem

For a large number of noninteracting particles (ideal gas) in a closed system of volume  $V$ , the Boltzmann distribution equations for average energy and entropy tell us that

$$E - TS = -T \log z.$$

The pressure of the system is defined as  $P := -\frac{\partial E}{\partial V}$ . It follows that  $PV = \kappa_B NT$ , or equivalently

$$P = \kappa_B \rho T \quad (\text{Ideal Gas Law})$$

where  $\rho$  is the density of the particles.

Now we will consider weakly interacting gas particles, with a potential energy given by  $u_0$ . For a small enough  $u_0$ , it suffices to consider only the first term in the Taylor polynomial expansion of the energy function (or equivalently, only 2 body interactions). We conclude that  $P \approx (\rho T + \frac{1}{2}\rho^2 u_0) \kappa_B$ . For more precision, we could consider up to N-body interactions, but typically  $\rho u_0 \ll T$  and the ideal gas laws are a sufficiently good approximation.

## The Ising Model

The *Ising model* approximate the Hamiltonian (energy) of a system consisting of  $N$  particles in a  $d$ -dimensional lattice by considering only interactions between neighboring particles (denoted  $\sigma_i$ ).

$$H(\sigma) = - \sum_{i=1}^N \sum_{j=1}^{i-1} J_{i,j} \sigma_i^2 \sigma_j^2 - \mu \sum_{i=1}^N h_i \sigma_i^2$$

where each  $\sigma_i^2 \in \{-1, 1\}$ , and  $J_{i,j} \neq 0$  if and only if  $\sigma_i$  and  $\sigma_j$  are neighbors. To “solve” the Ising model, one typically looks for the distribution of states  $\sigma$  as a function of inverse temperature ( $\beta$ ) or the minimum/maximum energy states.

In the simple case where the connections ( $J_{i,j}$ ) between all neighbors are equal to some constant  $J$ , and the energy for each particle’s spin ( $h_i$ ) is equal to some constant  $h$  we arrive at  $\sigma = \tanh((-2dJ\sigma + h)\beta)$ , where  $\sigma$  denotes the expected value of a discrete variable that is either 1 or  $-1$ . In the case of magnets,  $\sigma$  could represent the alignment of the magnetic particles or the presence of an attractive particle. In either case, we discover that due to the non-uniqueness of the solutions to this equation, there is a discontinuity in the surface of solutions that corresponds to a *phase transition* where  $\sigma$  snaps from  $\sigma \approx 0$  to  $\sigma \approx 1$ . The Ising model is appropriate for  $d \geq 2$  since for  $d = 1$ , it cannot predict phase transitions.