

## **Statistical Mechanics: An Introduction**

Statistical mechanics uses statistical methods to mathematically model the behavior of systems with many particles and many variables (degrees of freedom)— and therefore many approximations and calculations— which makes it difficult, if not impossible, to measure or model physically. The most common use for this explaining and quantifying macroscopic observations (e.g., laboratory results) with statistical mathematical models of the system in question. It works by using statistical ensembles: multiple probability functions for the same system.

The field describes the movement (“mechanics”) of a massive number of particles. It falls into the more general field of statistical physics, which deals with stochastic processes with a large number of particles or other variables, including in chemistry, biology, neurology, and sociology. Its main application deals with statistical mechanics, and the main application of statistical mechanics is in the field of thermodynamics, so often the term “statistical physics” or “statistical mechanics” refers directly to “statistical thermodynamics.” This paper will focus on historical significance with the Kinetic Theory of Gases and statistical thermodynamics. It is important to begin with the history of this field to understand its importance.

The origins of statistical mechanics lie in the Kinetic Theory of Gases, originally developed by Daniel Bernoulli in the early 1700s. Bernoulli was the first to believe that gases were a collection of many small particles moving at a very high speed, and he discovered the association between the kinetic energy of the particles and heat. Both are remarkable: first, because the Atomic Theory, formalized by John Dalton still had a few decades to come; and because the common theory for heat was that it was a form of matter called “caloric.” For these reasons, Bernoulli’s work on the Kinetic Theory of Gases was largely unnoticed, but it established the framework for later scientists, and the first to introduce a large system of rapidly moving particles, which is the exigence for statistical mechanics.

After the Caloric Theory was challenged, the Kinetic Theory of Gases lived on in sporadic works by scientists such as John Herapath and James Joule, until Rudolf Clausius (already reputed for his work with thermodynamics) took note of it in the 1850s, a century after Bernoulli. Clausius and Karl Krönig deduced that gas particles move randomly in straight lines until they hit other particles. This went against the common conception that gases move in

relatively predictable and uniform motion, but rather in random motion modelled by probability, another important pillar of statistical mechanics. Clausius derived the mean free path of a particle, or the average distance it travels before collision, in the equation:

$$l = \frac{3V}{4N\pi\sigma^2}$$

where  $l$  is the mean free path,  $N$  is the number of gas molecules,  $V$  is the volume, and  $\sigma$  is the approximate diameter of the gas molecules. This equation was refined by James Maxwell only a year later. Maxwell made another important step by assuming totally random motion of the particles, including velocities (before him, while the paths of the particles were assumed to be random, their speeds were assumed to be relatively constant). He developed the first probability distribution in physics for the velocities of the gas molecules:

$$f_0(v) = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}}$$

where  $v$  is the velocity,  $n$  is the density,  $m$  is the mass,  $k$  is Boltzmann's constant, and  $T$  is the temperature. Closely associated with Maxwell's work is Ludwig Boltzmann, who generalized Maxwell's equations for non-equilibrium systems. He developed a non-equilibrium single particle distribution function that predicts the number of particles at a given position, at a given velocity, and at a specific time. This single-particle distribution function was further used to describe other probabilistic phenomena, for example, his famous Boltzmann equation that describes how a fluid changes over time based on the movement of its particles, as well as the famous H-theorem (not shown below), which results in the following:

$$\frac{dH[f]}{dt} \leq 0$$

$$S(t) = -kH[f]$$

$$\frac{dS(t)}{dt} \geq 0$$

where  $S$  is the thermodynamic entropy. This describes the second law of thermodynamics, and has a basis in the work of Maxwell, as well as the foundational theories in randomness and large numbers of particles introduced by Clausius and Bernoulli.

A final notable chapter in the history of statistical mechanics is the generalization of statistical mechanics to more mechanical systems by Josiah Gibbs in the late 19th century. His work allowed the same reasoning applied in thermodynamics to also be applied to non-gaseous

and non-microscopic (macroscopic) systems. Later, after the invention of quantum mechanics, Gibbs' work was easily adapted to quantum systems in addition to the classical systems that Gibbs and his precursors had dealt with.

Gibbs' generalized view of statistical mechanics dealt with statistical *ensembles*: statistical distributions of all possible states of a system. These distributions represent the many possible outcomes of experiments or simulations of a similar system, and the mathematical model is created for the most likely state. These ensembles can also be used to describe equilibrium: the statistical mechanics definition of equilibrium is when the statistical ensemble of a system contains all of its possible past and future states; i.e., no evolution in a system.

Gibbs observed and delineated a few classes of statistical ensembles, which are defined by the dimensions kept constant:

**The Microcanonical (NVE) Ensemble:** This ensemble comprises a fixed number of particles (N), volume (V), and energy (E), which can be visualized by an insulated container.

**The Canonical (NVT) Ensemble:** This ensemble comprises a fixed number of particles (N), volume (V), and temperature (T), but a variable amount of energy, which can be visualized by a non-insulated container connected to an arbitrarily large "heat bath" for energy transfer.

**The Grand Canonical ( $\mu$ VT) Ensemble:** This ensemble comprises a variable number of particles and energy, which can be visualized by an open container. Instead, what is constant is the chemical potential ( $\mu$ ), volume (V), and temperature (T), which are necessary for calculations to be made.

Two more main classes of statistical ensembles were discovered after Gibbs, the isoenthalpic-isobaric (NpH) and isothermal-isobaric (NpT) ensembles. These can be represented as the weighted sum of a similar canonical ensemble.

For the sake of brevity, only a short discussion of the canonical ensemble will be discussed, as it is often used for its simplicity (its constants are easier to measure). Each possible microstate is assigned a probability:

$$P = e^{\frac{E-F}{kT}}$$

where  $P$  is the probability,  $F$  is the Helmholtz free energy,  $k$  is Boltzmann's constant,  $E$  is the energy, and  $T$  is the absolute temperature. It can describe a system of any size in equilibrium with a heat bath, as long as the heat bath is considerably large and there is no other energy interaction except with the heat bath. If these conditions are met, certain properties arise, such as that the canonical ensemble average (predicted state) has the minimum free energy and the highest entropy of any state in the ensemble, which makes sense due to the fundamental tendency of systems to reach higher-entropy and lower-energy states. The canonical ensemble also is associated with several equations that apply to all such systems, such as:

$$\text{Average pressure: } \langle p \rangle = - \frac{\partial F}{\partial V}$$

$$\text{Gibbs entropy: } S = - \frac{\partial F}{\partial T}$$

$$\text{First law of thermodynamics: } d\langle E \rangle = TdS - \langle p \rangle dV$$

Together, these equations often describe a generalized Boltzmann distribution, many of which were generalized by Gibbs. The generalized Boltzmann distribution is the most applicable of the statistical ensembles, applying to many types of systems (gas particles, electromagnetic modes in cavities, polymers), but there also exists the Ising model that uses the canonical ensemble and is important for particle interactions in ferromagnetism and phase transitions.

Statistical physics has led to quantitative descriptions of superfluidity, superconductivity, turbulence, structures of different phases of matter, liquid crystals, and critical phenomena. Many modern particle experiments are based solely on statistical, mathematical representations. It is in this field that scientists have been able to really apply physics where numbers could not work.

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