

# **Lesson 2- Connections**

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## Statement

Statistical Mechanics is only **rigorous** in the **thermodynamic limit**, i.e.

$$N \rightarrow \infty$$

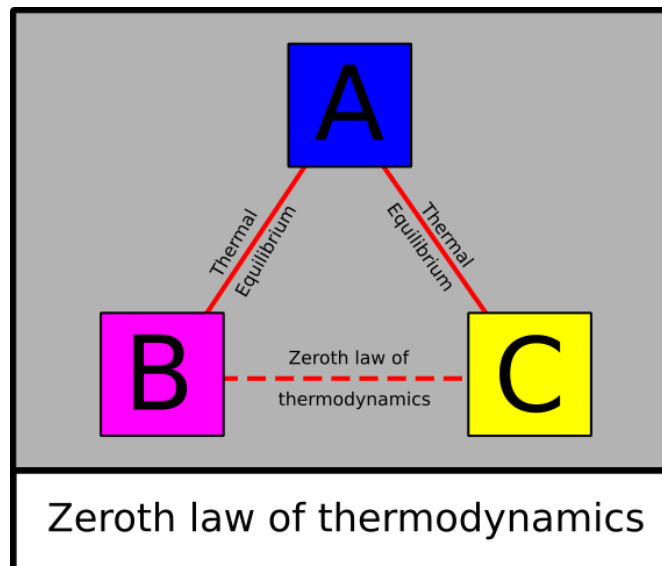
$$V \rightarrow \infty$$

$$\rho = \frac{N}{V} \quad \text{finite}$$

is essentially a consequence of the central limit theorem of probability theory. The internal energy of a gas of  $N$  molecules is the sum of  $N$  contributions, each of which is approximately independent, and so the central limit theorem predicts that the ratio of the size of the fluctuations to the mean (variance) is of order  $1/\sqrt{N}$ .

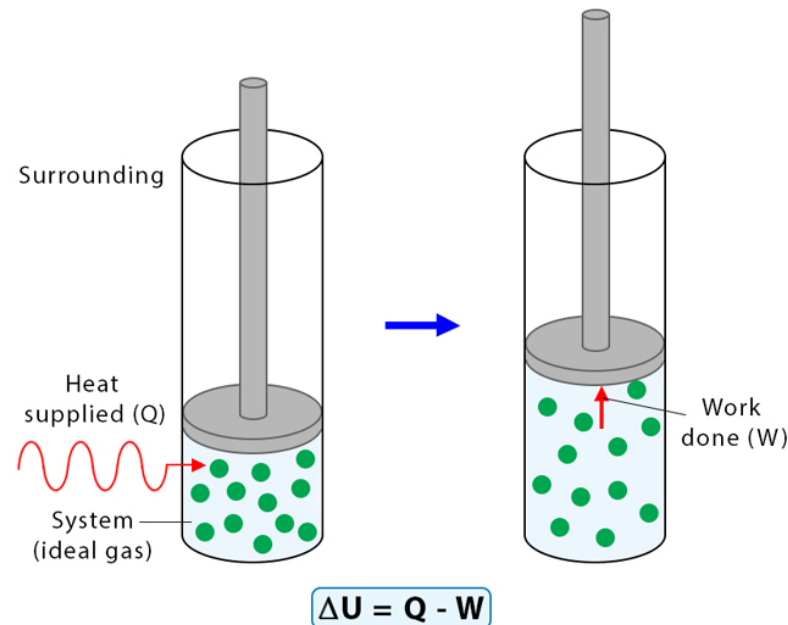
## Principles of thermodynamics

**Zeroth Law of Thermodynamics:** If two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other. This principle allows us to define temperature as a transitive, measurable quantity.



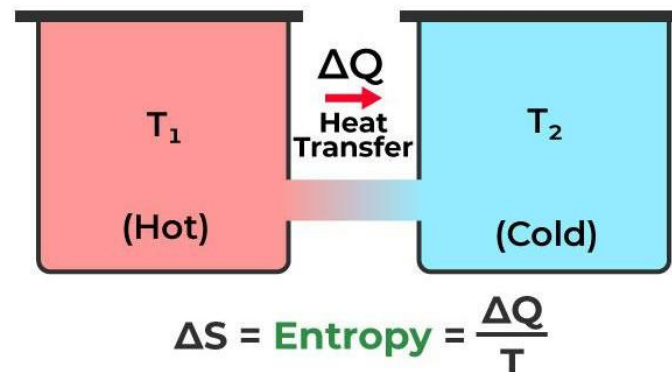
## Principles of thermodynamics

**First Law of Thermodynamics:** Energy can neither be created nor destroyed, only transformed. Mathematically, this is expressed as  $\Delta U = Q - W$ , where  $\Delta U$  is the change in internal energy,  $Q$  is the heat added to the system, and  $W$  is the work done by the system on its surroundings.



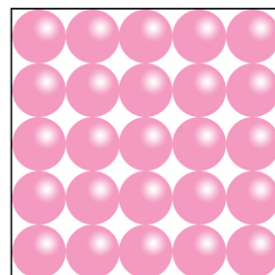
## Principles of thermodynamics

**Second Law of Thermodynamics:** In any energy exchange, if no energy enters or leaves the system, the potential energy of the state will always be less than that of the initial state, often referred to as entropy  $S$  increasing. This can be formally stated using the Clausius inequality:  $\delta Q \leq TdS$ , where  $\delta Q$  is the differential heat transfer into a system undergoing a reversible cycle, and  $T$  is the temperature at which the heat transfer occurs.

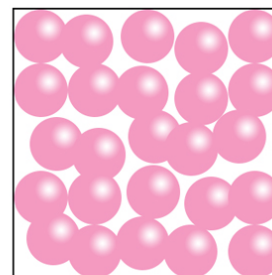


## Principles of thermodynamics

**Third Law of Thermodynamics:** As the temperature of a system approaches absolute zero ( $T \rightarrow 0$ ), its entropy  $S$  tends towards a constant minimum value. Implications: first it signifies the impossibility of reaching absolute zero in a finite number of thermodynamic operations; second, it provides a theoretical foundation for the concept of entropy approaching a minimum value, which is crucial for understanding the thermodynamic behavior of systems at low temperatures.



$$T = 0$$
$$S = 0$$



$$T > 0$$
$$S > 0$$

## Principles of thermodynamics

The principles of thermodynamics are **empirical laws**, grounded in experimental observations and validated through a vast range of applications. While they are not "proven" in a mathematical sense, they serve as **fundamental axioms** for the field of thermodynamics.

## Extensive and intensive variables

**Extensive** variables are additive and proportional to the size of the system. Mathematically, for a system divided into  $n$  subsystems, an extensive variable  $X$  satisfies the relation:

$$X = \sum_i X_i$$

Where  $X_i$  represents the value of the variable for the  $i^{th}$  subsystem. Examples include mass  $m$ , volume  $V$ , internal energy  $U$ , and entropy  $S$ .



## Extensive and intensive variables

**Intensive** variables are invariant under the division of the system. They do not scale with the size but are instead properties inherent to the system's state. For a system divided into  $n$  subsystems, an intensive variable  $Y$  satisfies:

$$Y = Y_1 = Y_2 = \dots = Y_n$$

Where  $Y_i$  is the value of  $Y$  in the  $i^{th}$  subsystem. Examples include temperature  $T$ , pressure  $P$ , and chemical potential  $\mu$ .

## Extensive and intensive variables

In many cases, intensive variables can be derived as derivatives of extensive variables with respect to another extensive variable, holding certain variables constant. For example, temperature is related to internal energy  $U$  and entropy  $S$  as:

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

where  $V$  is the volume and  $N$  is the number of particles, both held constant.

## Generalized fields

Equivalently to classical mechanics, in thermodynamics we can define generalized fields  $X_i$  from intensive variables  $\xi_i$  in such a way that:

$$\delta W = \sum_i X_i d\xi_i$$

this variables are related through Legendre transforms.

Reminder: The **Legendre transform** of a function  $\mathbf{f}(\mathbf{x})$  with respect to  $x$  and its conjugate variable  $p = \frac{df}{dx}$  is given by:

$$\mathbf{g}(\mathbf{p}) = \mathbf{p}\mathbf{x} - \mathbf{f}(\mathbf{x})$$

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## Generalized fields

We can use the Legendre transform to switch among different potentials. Let us start with the second law of thermodynamics

$$dS = \frac{dU}{T} + \frac{\delta W}{T} = \frac{dU}{T} + \frac{\sum_i X_i d\xi_i}{T}$$

then:  $\left(\frac{\partial S}{\partial U}\right)_{\xi_i} = \frac{1}{T} \quad \left(\frac{\partial S}{\partial \xi_i}\right)_{\xi_{j \neq i}, T} = \frac{X_i}{T}$

for example, if we consider the extended work

$$\sum_i X_i d\xi_i = -pdV + \mu dN$$

## Generalized fields

We can express the internal energy potential as

$$dU = TdS - pdV + \mu dN$$

note that this equation implies that the entropy  $S(U, N, V)$  is an **extensive** magnitude.

Proof: if a magnitude is extensive it must be homogeneous of 1st order:  $S(\lambda U, \lambda N, \lambda V) = \lambda S(U, N, V)$  deriving on  $\lambda$

$$\frac{\partial S}{\partial \lambda U} U + \frac{\partial S}{\partial \lambda N} N + \frac{\partial S}{\partial \lambda V} V = S$$

## Generalized fields

The former identity is valid  $\forall \lambda$ , in particular for  $\lambda = 1$

$$S = \frac{U}{T} + \frac{VP}{T} - \frac{\mu}{T}$$

coherent with the fact that

$$U = TS - pV + \mu N$$

This potential will be derived using statistical mechanics later on.

## From potential to potential using Legendre transform

**The internal energy**  $U$  serves as the foundational thermodynamic potential and is naturally expressed in terms of entropy  $S$ , volume  $V$ , and the number of particles  $N$ :

$U = TS - pV + \mu N$  in differential form

$$dU = TdS - pdV + \mu dN$$

**The Helmholtz free energy**  $F$  is derived from  $U$  by performing a Legendre transformation with respect to the entropy  $S$ , replacing it with its conjugate variable, temperature  $T$ . Mathematically, this transformation is expressed as:

$F(T, V, N) = U(S, V, N) - TS$ . The differential form for  $F$  after the transformation becomes:

$$dF = -SdT - pdV + \mu dN$$

## From potential to potential using Legendre transform

**The Gibbs free energy**  $G$  is obtained from  $U$  by a Legendre transformation with respect to both  $S$  and  $V$ , introducing their conjugate variables  $T$  and  $P$ , respectively:

$$G(T, P, N) = U(S, V, N) - TS + PV$$

The differential form for  $G$  becomes:

$$dG = -SdT + VdP + \mu dN$$

**The enthalpy**  $H$  is derived from  $U$  via a Legendre transformation with respect to  $V$ , replacing it with its conjugate variable, pressure  $P$ :  $H(S, P, N) = U(S, V, N) + PV$

The differential form for  $H$  is:

$$dH = TdS + VdP + \mu dN$$



## Virial theorem

We define the virial of a system of  $n$  particles as:

$G \equiv \sum_i \mathbf{p}_i \cdot \mathbf{r}_i$  where  $i$  sums over all particles. The time

derivative of  $G$  is  $\frac{dG}{dt} = \sum_i \mathbf{p}_i \cdot \dot{\mathbf{r}}_i + \sum_i \dot{\mathbf{p}}_i \cdot \mathbf{r}_i$

note that  $\sum_i \mathbf{p}_i \cdot \dot{\mathbf{r}}_i = \sum_i m \dot{\mathbf{r}}_i \cdot \dot{\mathbf{r}}_i = \sum_i m v^2 = 2T$ , and the

second term is  $\sum_i \dot{\mathbf{p}}_i \cdot \mathbf{r}_i = \sum_i \mathbf{F}_i \cdot \mathbf{r}_i$  thus

$$\frac{dG}{dt} = 2T + \sum_i \mathbf{F}_i \cdot \mathbf{r}_i$$

## Virial theorem

The time average over a period  $\tau$  is

$$\frac{1}{\tau} \int_0^\tau \frac{dG}{dt} dt = \frac{G(\tau) - G(0)}{\tau} = \langle 2T \rangle + \left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle$$

Note that, if the positions and velocities of all the particles remain finite, then there is an upper bound to  $G$ . This implies

that choosing  $\tau \rightarrow \infty$  means that  $\frac{G(\tau) - G(0)}{\tau} \rightarrow 0$ , then

$$\langle T \rangle = -\frac{1}{2} \left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle \text{ note that averages here are}$$

**time averages.**

## Ergodic hypothesis

Averaging a system over a long time period may be equal to averaging the system over the ensemble. This is the ergodic hypothesis. Mathematically it can be written as

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} dt \rightarrow \lim_{N \rightarrow \infty} \frac{1}{N} \sum_i^N$$

If a bound system has a huge number of particles ( $N \rightarrow \infty$ ), it is equivalent to seeing the system over a long period of time ( $\tau \rightarrow \infty$ ).

## Ergodic hypothesis

Thus, we can apply the virial theorem to a **galaxy** by taking the mean of the kinetic and potential energy of all stars in the galaxy in a given instant. According to the ergodic hypothesis, it is not necessary in this case to take the mean of the kinetic and potential energy over a very long period of time. Since the time scales for changes for such huge systems is very long, it is much easier to simply take the average over all stars. The ergodic theorem thus says that we can replace the mean value from being a time average to be an average over all bodies in the system.

## Dark Matter

For a gravitationally bound system like a galaxy or galaxy cluster, the Virial Theorem provides a relation between the time-averaged total kinetic energy  $\langle T \rangle$  and the time-averaged total potential energy  $\langle U \rangle$  as  $2\langle T \rangle = -\langle U \rangle$ .

One can empirically measure the velocities of stars or galaxies within the cluster to estimate the kinetic energy  $T$ . The distribution of visible matter, usually through optical or radio telescope data, gives an estimate of the gravitational potential  $U$ . When the Virial Theorem is applied using just the visible matter, inconsistencies are observed. The measured velocities are much higher than what would be expected based on the gravitational potential due to the visible matter alone.

## Dark Matter

These discrepancies imply that there must be additional, unseen mass contributing to the gravitational potential  $U$  to reconcile with the observed velocities and hence the kinetic energy. This unseen mass, which doesn't interact with electromagnetic radiation in a manner similar to ordinary (baryonic) matter, is what we refer to as "dark matter."

