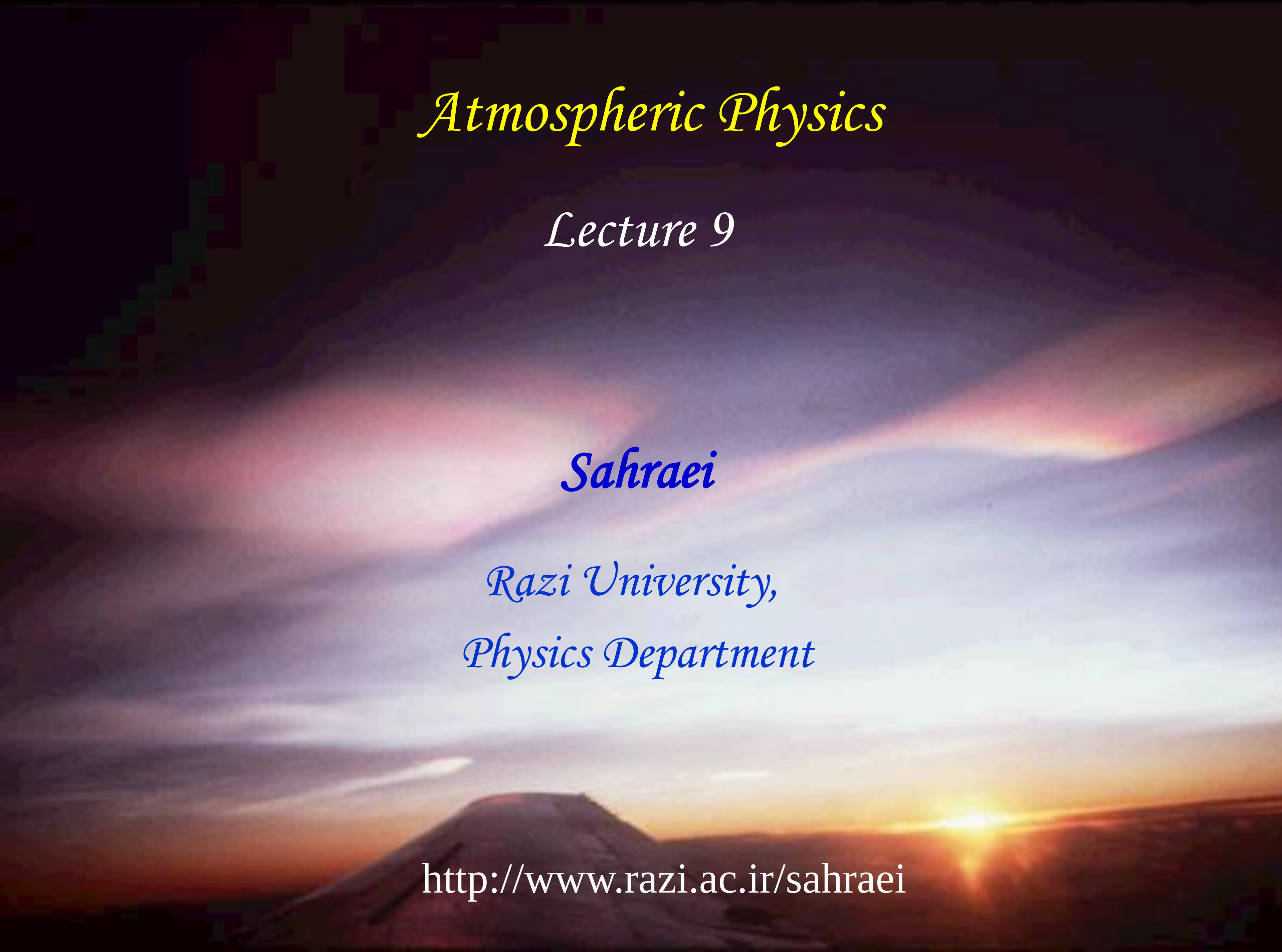


Atmospheric Physics

Lecture 9

Sahraei

Razi University,
Physics Department

http://www.razi.ac.ir/sahraei

Isentropic process فرآیندهای بی درو برگشت پذیر

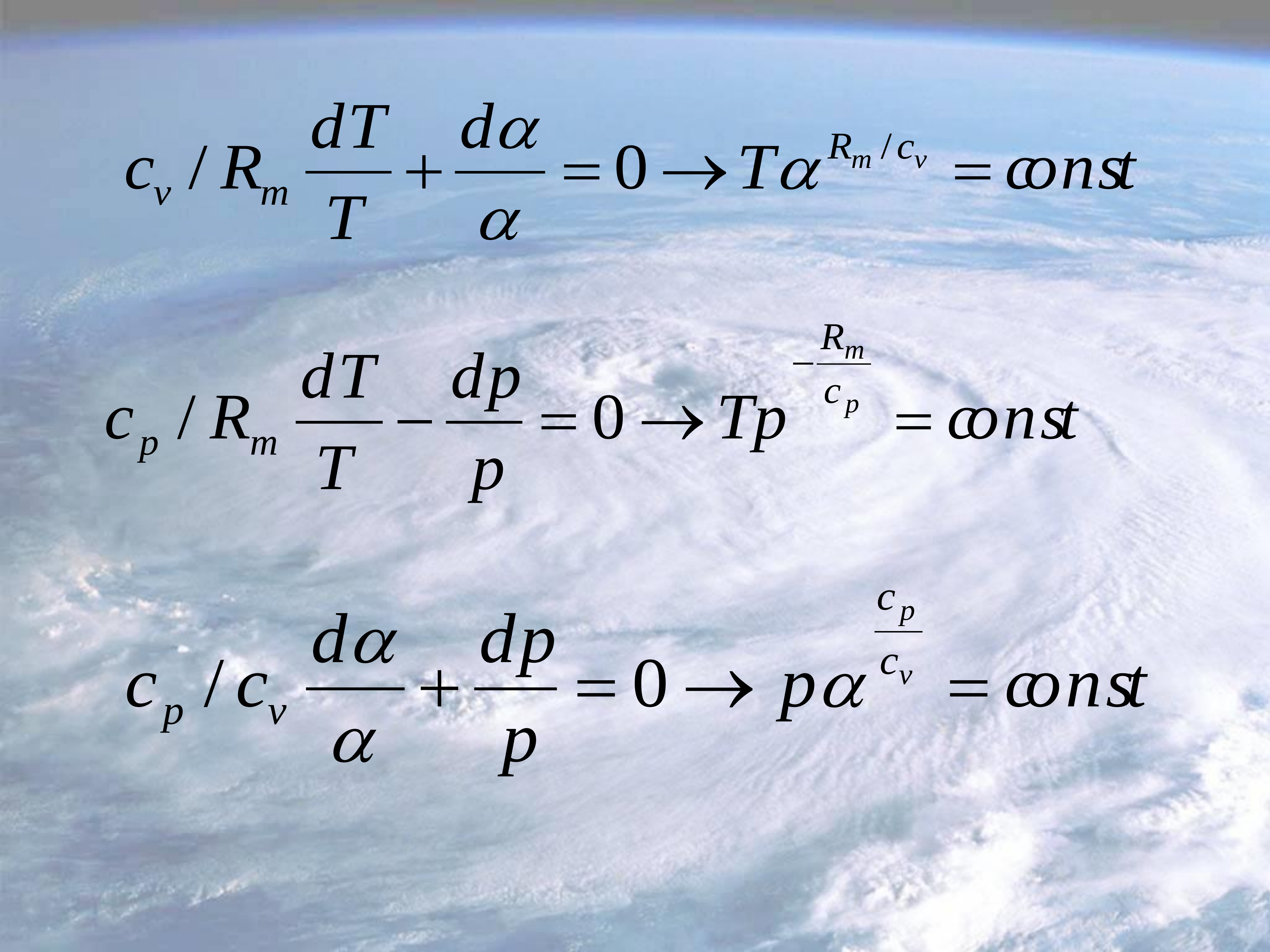
An adiabatic process which is also reversible is called an isentropic process.

$$s = const \rightarrow ds = dh = 0$$

$$dh = du + p d\alpha$$

$$c_v dT + p d\alpha = 0$$

$$\frac{dh}{T} = c_v \frac{dT}{T} + R_m \frac{d\alpha}{\alpha}$$



$$c_v / R_m \frac{dT}{T} + \frac{d\alpha}{\alpha} = 0 \rightarrow T\alpha^{R_m / c_v} = const$$

$$c_p / R_m \frac{dT}{T} - \frac{dp}{p} = 0 \rightarrow Tp^{-\frac{R_m}{c_p}} = const$$

$$c_p / c_v \frac{d\alpha}{\alpha} + \frac{dp}{p} = 0 \rightarrow p\alpha^{\frac{c_p}{c_v}} = const$$

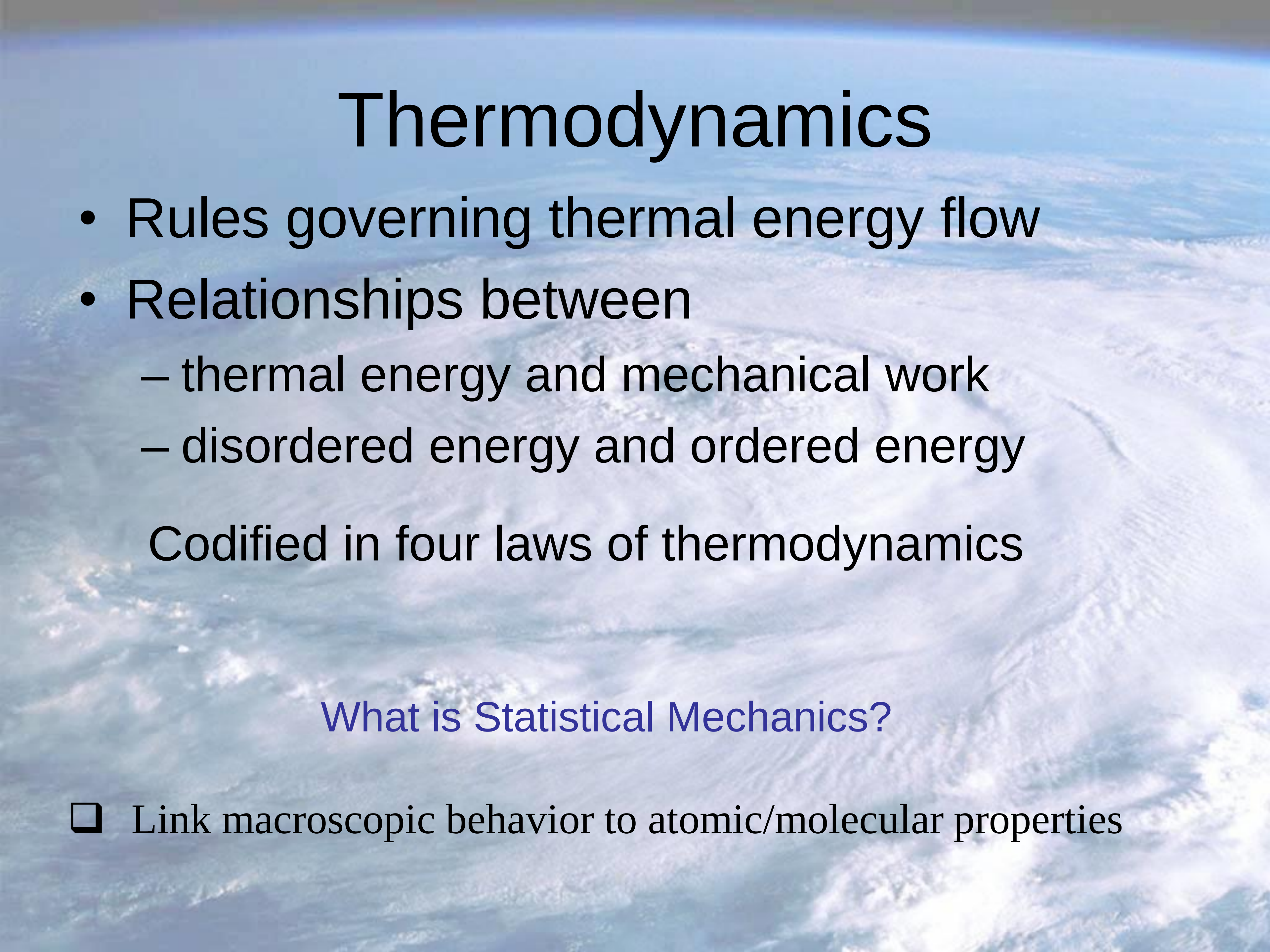
Potential Temperature

The *potential temperature* (θ) is defined as that temperature which would result if the air were brought isentropically to a standard pressure p_0.

$$T_p^{-\kappa} = \theta p_0^{-\kappa} = const$$

$\theta = T(p_0 / p)^{\kappa}$ where κ represents R_m / c_p

p_0 is usually taken as 100 kPa (1000 mb).



Thermodynamics

- Rules governing thermal energy flow
- Relationships between
  - thermal energy and mechanical work
  - disordered energy and ordered energy

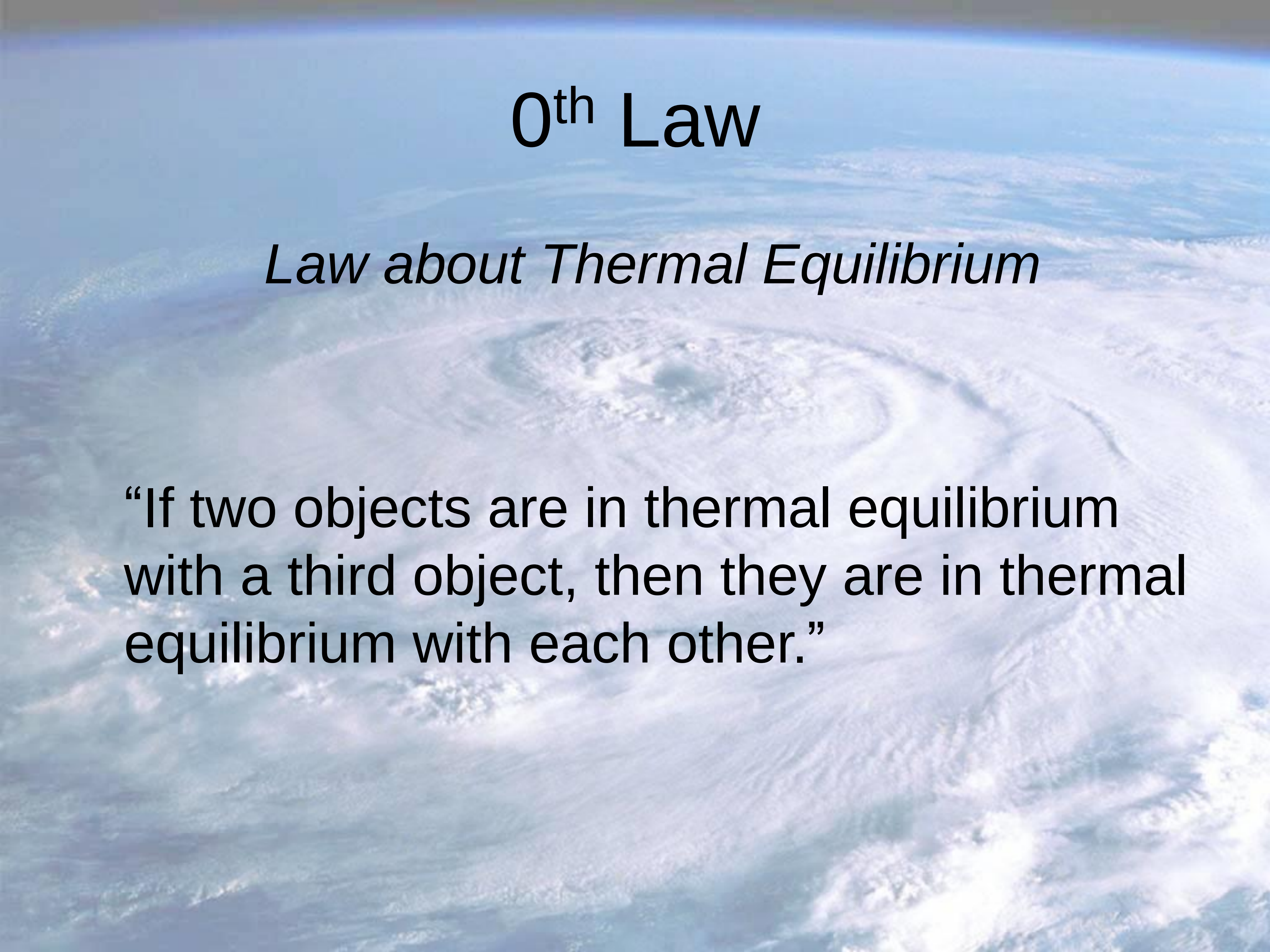
Codified in four laws of thermodynamics

What is Statistical Mechanics?

❑ Link macroscopic behavior to atomic/molecular properties

0th Law

Law about Thermal Equilibrium



“If two objects are in thermal equilibrium with a third object, then they are in thermal equilibrium with each other.”

1st Law

Law about Conservation of Energy

“Change in internal energy equals heat in minus work out”

where:

Internal energy: thermal + stored energies

Heat in: heat transferred into object

Work out: external work done by object

Entropy and the Laws of Thermodynamics

- The second law is controlled by the concept of entropy

Order versus Disorder

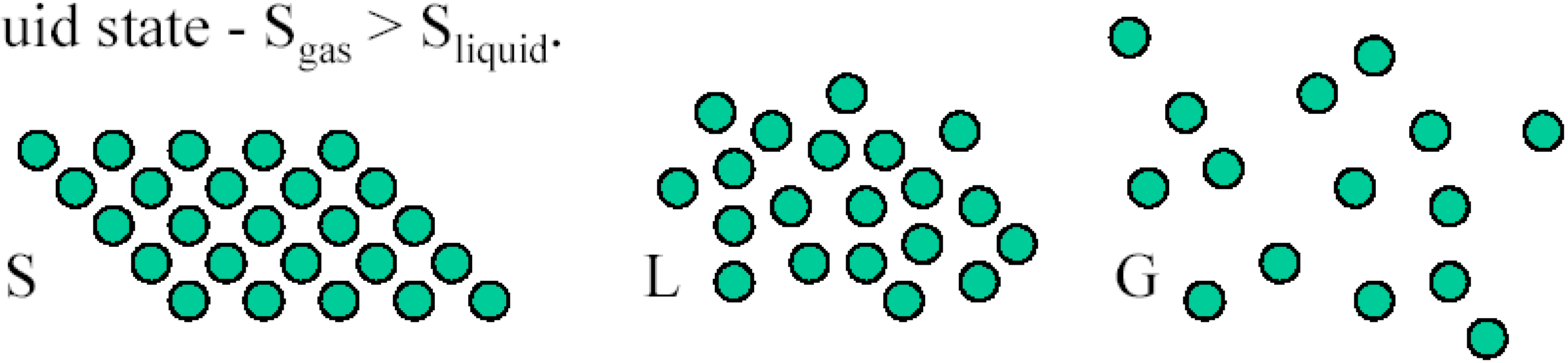
- It is easy to convert ordered energy into thermal (disordered) energy
- It is hard to converting thermal energy into ordered energy
- Statistically, order to disorder is one-way

Entropy

- Entropy is measure of object’s disorder
- Includes both thermal and structural disorders

Intuitive consideration:

In a crystal atoms are vibrating about their regularly arranged lattice sites, in a liquid atomic arrangement is more random – $S_{liquid} > S_{solid}$. Atomic disorder in gaseous state is greater than in a liquid state - $S_{gas} > S_{liquid}$.



Melting at constant pressure requires absorption of the latent heat of melting, $q = \Delta H_m$, therefore $\Delta S_m = \Delta H_m / T_m$

- **the increase in the entropy upon melting correlates with the increase in disorder.**

$$dh = du + p\,d\alpha$$

$$dh = c_v\,dT + p\,d\alpha$$

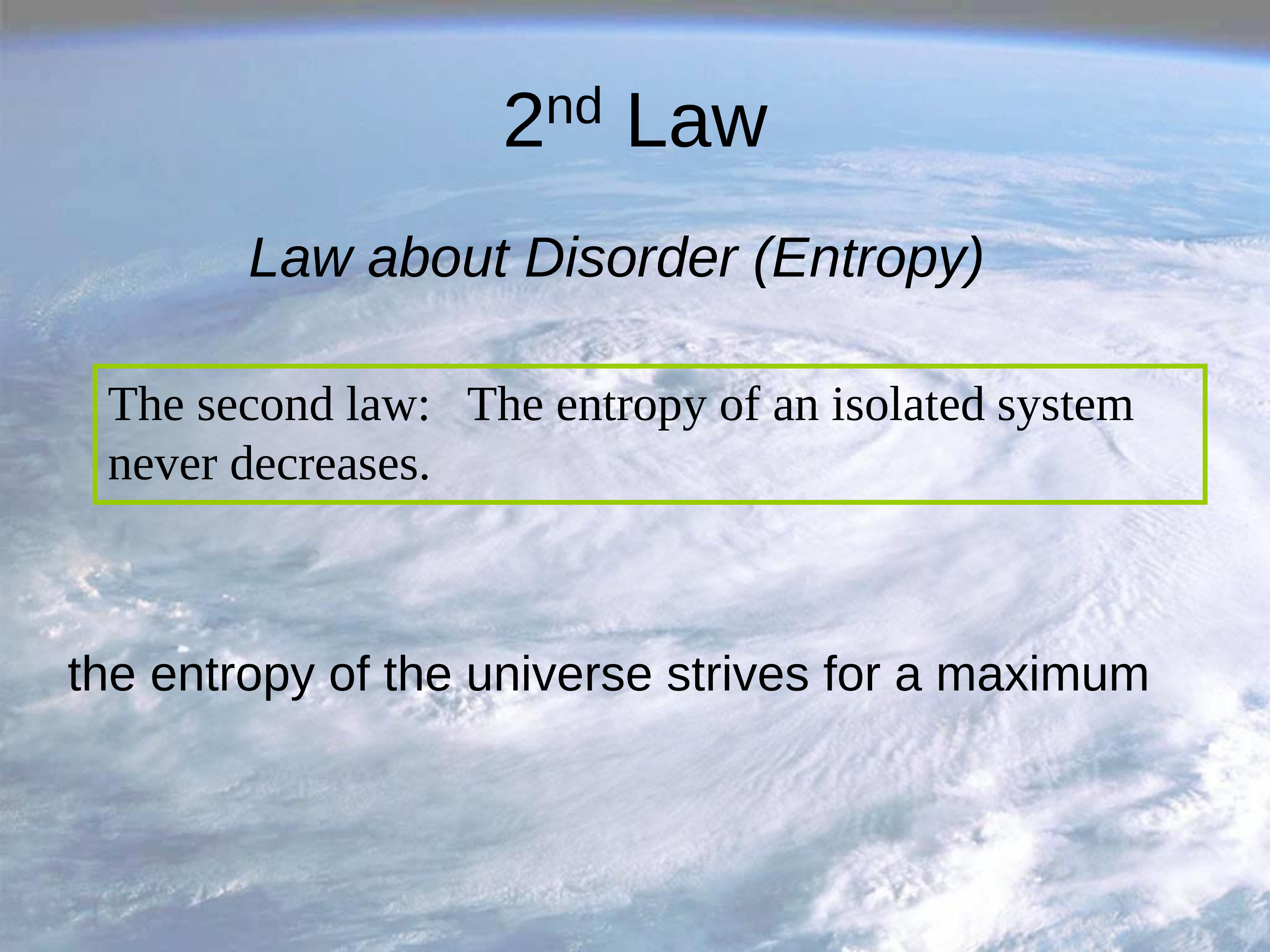
$$p\alpha = R_m T \rightarrow p\alpha\,d\alpha = R_m T\,d\alpha$$

$$\frac{dh}{T} = c_v \frac{dT}{T} + R_m \frac{d\alpha}{\alpha}$$

$$\frac{dh}{T} = ds$$

$$\oint ds = 0$$

There exists a state function *S* called the entropy. This is such that, for a reversible process,



2nd Law

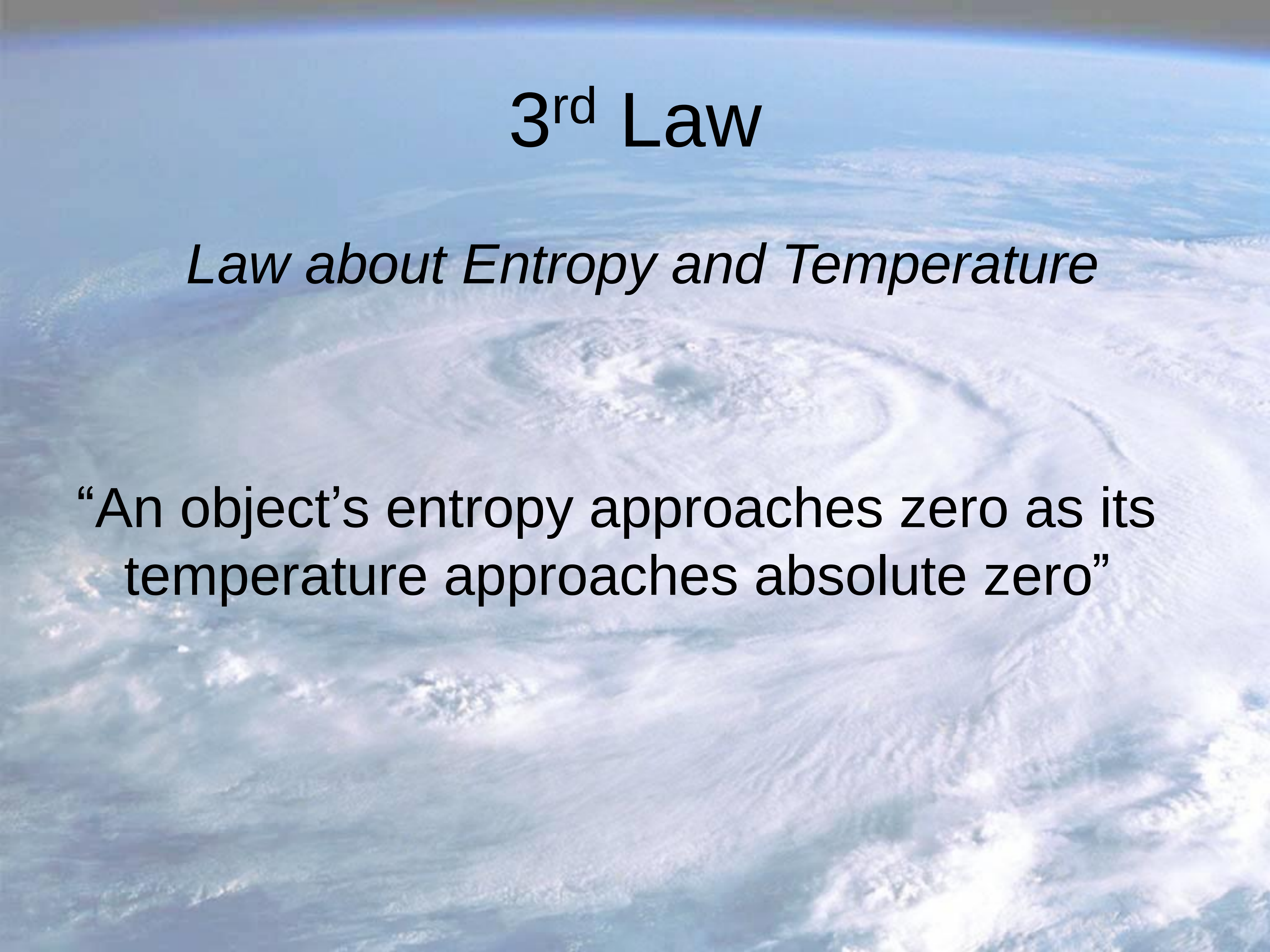
Law about Disorder (Entropy)

The second law: The entropy of an isolated system never decreases.

the entropy of the universe strives for a maximum

More on the 2nd Law

- According to the 2nd Law:
  - Entropy of a thermally isolated system can’t decrease
  - But entropy can be redistributed within the system
  - Part of the system can become hotter while another part becomes colder!



3rd Law

Law about Entropy and Temperature

“An object’s entropy approaches zero as its temperature approaches absolute zero”

Thermodynamic probability

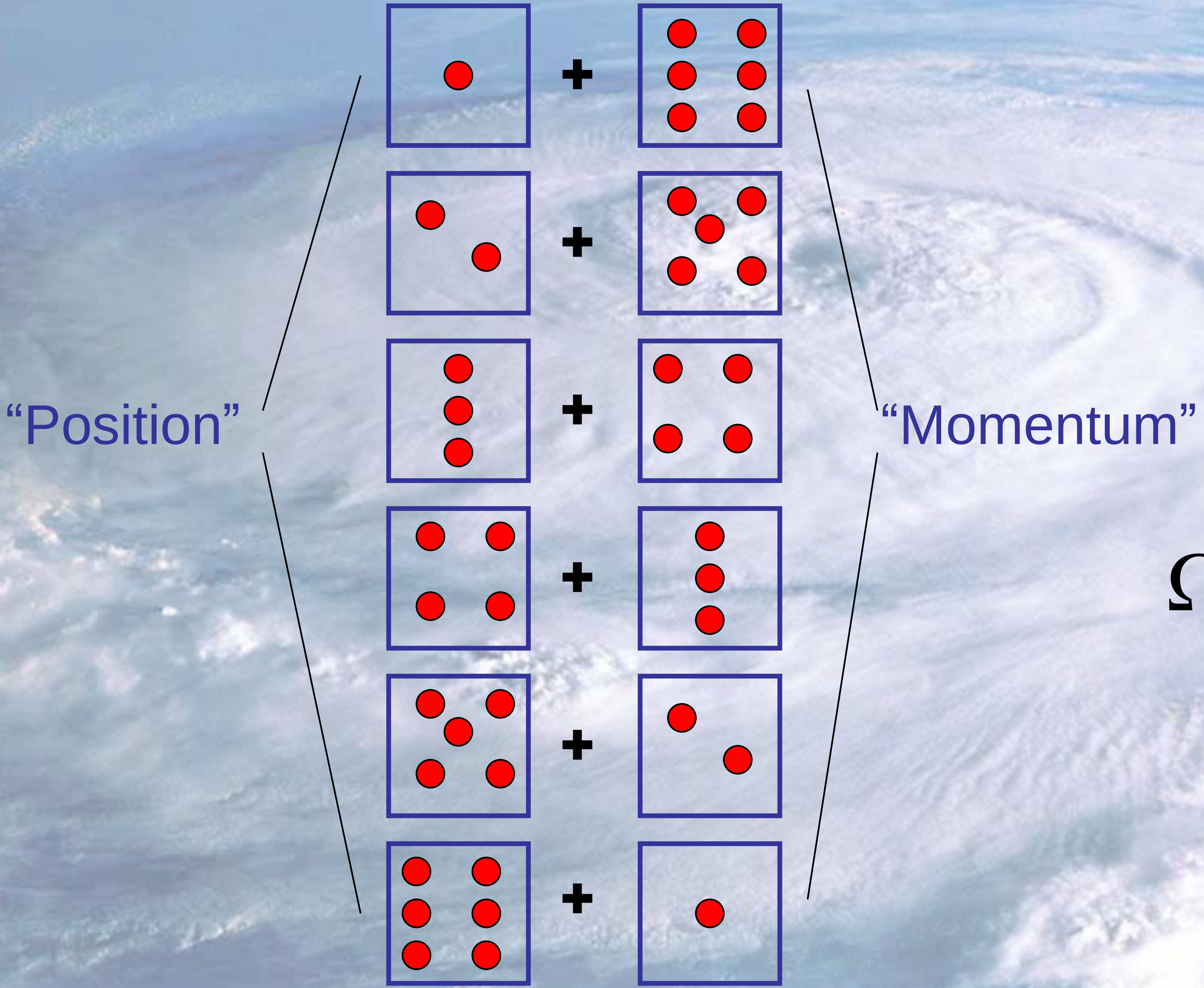
- Statistical thermodynamics uses a mathematical description of the distribution of particle **positions** and **speeds** to calculate the state variables for a system and to obtain values of the state functions, such S.

- Several **different** arrangements of molecules in phase space can correspond to the **same** bulk state (P, V, T).

- The number of arrangements of molecules for a particular state of the systems is called the **thermodynamic probability**, Ω.

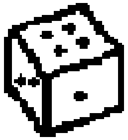
Analogy for Thermodynamic Probability

“State” of the system = sum of dice = 7



Ω = 6

Example for making it intuitive (rolling dice)



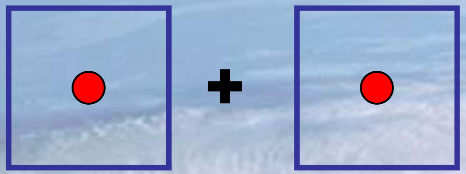
Macrostate – the total of the dice.

Each die have 6 microstates, the system of 2 dices has 6×6=36 microstates, a system of N dice has 6^N microstates.

For two dice there are 6 ways/microstates to get macrostate 7, but only one microstate that correspond to 2 or 12. The most likely macrostate is 7. For a big number N of dice, the macrostate for which the number of possible microstates is a maximum is 3.5×N

Analogy for Thermodynamic Probability

“State” of the system = sum of dice = 2



$\Omega = 1$

- Conclude that a “state” of 7 is more likely to be found as it has a higher probability, Ω.
- In a “real” system, each state (P_i, V_i, T_i) will have a certain Ω_i.
- As one mole contains ~10^{23} molecules, tends to be a very large number!
- The equilibrium state of a system is most likely and hence must have the largest Ω.

Microstates and Macrostates

A **macroscopic state** of a system can be described in terms of a few macroscopic parameters, e.g. P, T, V. The system can be also described in terms of **microstates**, e.g. for a system of N particles we can specify coordinates and velocities of all atoms.

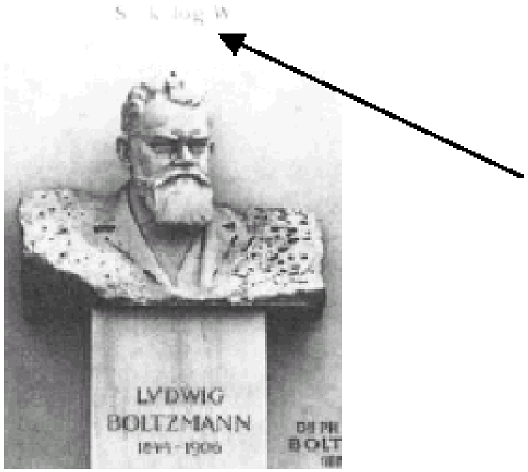
The 2nd law can be stated as follows: **The equilibrium state of an isolated system is the one in which the number of possible microscopic states is the largest.**

An isolated thermodynamic system is similar – **thermal fluctuations** do the shaking, the macrostate corresponds to **the largest number of microstates**. Actually, the system of dice is closer to a quantum system with discrete states. In the classical case the states form a continuum and we have to replace the sum over states by integrals over phase space.

Statistical interpretation of entropy

If we combine two systems, the number of microstates multiply (remember 6×6=36 for two dice). At the same time we know that entropy is an extensive quantity, $S_{A+B} = S_A + S_B$, and if we want to relate enthalpy to the number of microstates, we have to make sure that this equation is satisfied.

If we take logarithm of the number of microstates, the logarithms adds when we put systems together. The quantity maximized by the second law can be defined then by equation written on Ludwig Boltzmann's tombstone in Vienna:



$S = k_B \ln \Omega$

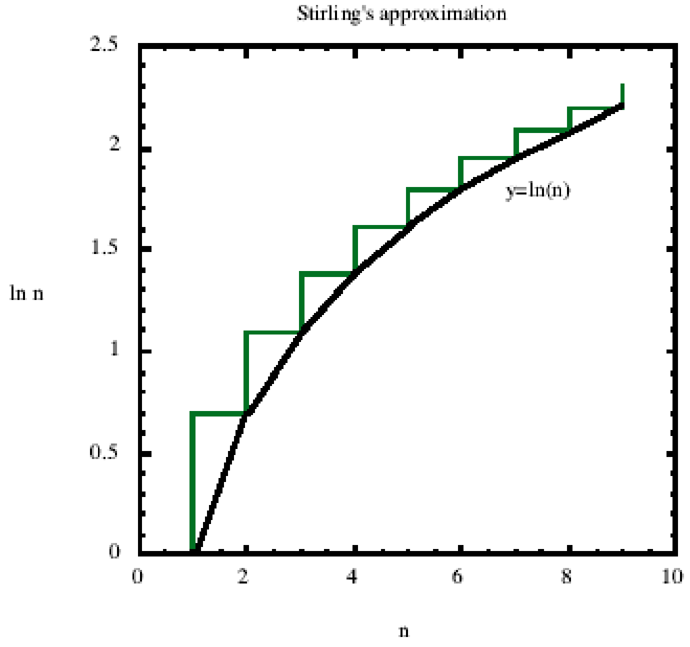
where Ω is the number of microstates, k is the Boltzmann constant (it is the same constant that relates kinetic energy to temperature, but it was first introduced in this equation), and S is the entropy.

The 2nd law can be restated again: **An isolated system tent toward an equilibrium macrostate with maximum entropy, because then the number of microstates is the largest.**

The entropy is related to the number of ways the microstate can rearrange itself without affecting the macrostate.

and the computation becomes *much* more challenging. First we need Stirling's approximation for $\ln n!$ Notice that

$$\ln n! = \ln 1 + \ln 2 + \ln 3 + \ldots + \ln n = \sum_{k=1}^{n} \ln k$$



This equation is the area under the step curve between 1 and n. When n is large this step curve is well approximated by the curve $y = \ln n$, Thus

$$\sum_{k=1}^{n} \ln k \approx \int_1^n \ln x \, dx = \left[x \ln x - x\right]_1^n = n\,\mathrm{l}$$

and for very large n the one can be neglected. So we can use Stirling's approximation and write

$$\ln n! \approx n \ln n - n.$$