

# Entropy: is it what we think it is and how should we teach it?

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## We owe our current view of entropy to Gibbs:

“For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the system that do not alter its energy, the variation of its entropy shall vanish or be negative.”

Equilibrium of Heterogeneous Substances, 1875

## And Maxwell:

“We must regard the entropy of a body, like its volume, pressure, and temperature, as a distinct physical property of the body depending on its actual state.”

Theory of Heat, 1891

## Clausius:

Was interested in what he called “internal work”  
– work done in overcoming inter-particle forces;

Sought to extend the theory of cyclic processes  
to cover non-cyclic changes;

Actively looked for an equivalent equation to  
the central result for cyclic processes;

$$\int \frac{dQ}{T} \geq 0$$

## Clausius:

In modern thermodynamics the sign is negative, because heat must be extracted from the system to restore the original state if the cycle is irreversible .

The positive sign arises because of Clausius' view of heat; not caloric but still a property of a body

The transformation of heat into work was something that occurred within a body – led to the notion of “equivalence value”,  $Q/T$

## Clausius:

Invented the concept “disgregation”,  $Z$ , to extend the ideas to irreversible, non-cyclic processes;

$$TdZ \geq dI + dW$$

Inserted disgregation into the First Law;

$$dQ + dH + TdZ \geq 0$$

## Clausius:

Changed the sign of  $dQ$ ; (originally  $dQ=dH+AdL$ ;  $dL=dl+dW$ )

Derived;

$$\int \frac{dQ + dH}{T} + \int dZ \geq 0$$

Called;

$$\int \frac{dH}{T} + dZ$$

the entropy of a body.

**Disgregation:** Measures “the force of the heat”.

‘In order ... to determine the force of the heat we must evidently not consider the resistance which actually is overcome, but that which can be overcome’ - (Clausius, 1862)

‘The law does not speak of the work which the heat actually *does*, but that which it *can do*. Similarly, in the first form of the law ... it is not of the resistances which the heat overcomes but of those which it *can overcome* that mention is made’ - (Clausius, 1862)

Therefore:

$$dS \geq \frac{dQ}{T}$$

But what does the inequality really mean?

$$TdS \geq dQ + d\Phi$$

$d\Phi$  has the units of energy but is not  $dU$ ,  $dQ$ ,  $dW$  or any combination of them!



## Moreover:

Clausius applied the concept of disgregation to the ideal gas.

There are no inter-particle forces, and therefore no internal work.

There is no need to introduce the disgregation.

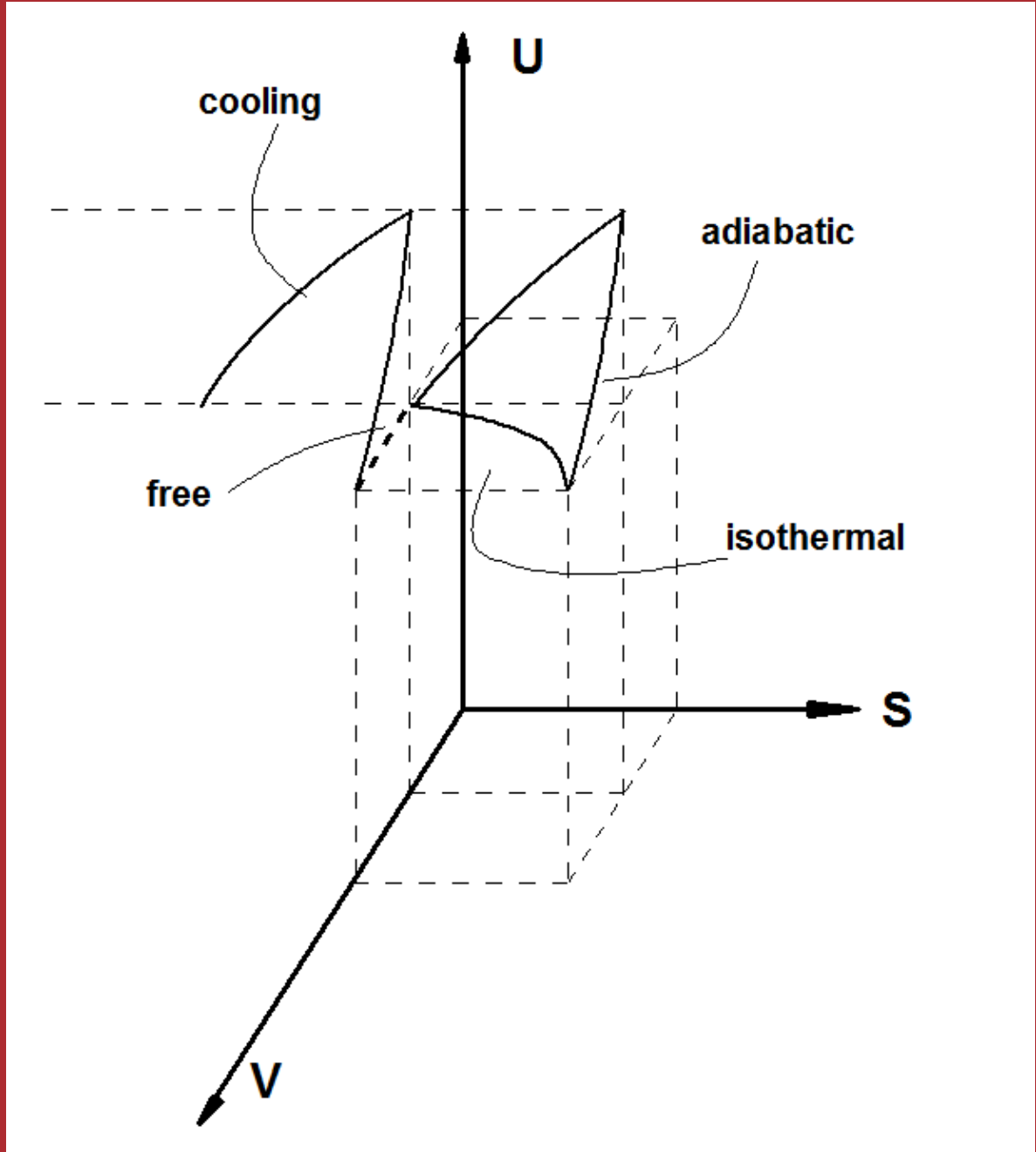
In a free expansion:

$$TdZ = pdV$$

$$dW = dQ = 0$$

$$dS = dZ > 0$$

Some property of the gas with units of energy is changing, but  $pdV$  is a fictitious work term that has its origins in the notion of “force of the heat”.



## The microscopic view

The emphasis in thermodynamics shifted away from engines and cyclic processes to the microscopic.

“If we define thermodynamics, as I think we may now do, as the investigation of the dynamical and thermal properties of bodies, ... all speculations as to how much of the energy in a body is in the form of heat are quite out of place.”

Maxwell, *Tait's Thermodynamics*, 1878

# Statistical mechanics: canonical distribution

Often given a physical interpretation: the probability of finding a small system in contact with a reservoir in a given energy state.

$$k_B \ln[\Omega(E - E_S)] = S_R(E - E_S) = S_R(E) - E_S \left[ \frac{\partial S_R(E_R)}{\partial E_R} \right]_{E_R=E}$$

$$\frac{\partial S_R(E_R)}{\partial E_R} = \frac{1}{T}$$

$$p(E_i) = \frac{1}{Z} e^{\frac{-E_i}{kT}}$$

$$S = -k_B \ln Z + \frac{\bar{E}}{T}$$

The entropy depends on parameters that do not themselves fluctuate

## Statistical mechanics and information theory:

The work of Jaynes in particular and Tribus has attempted to explain thermodynamics in terms of information theory as developed by Shannon.

Jaynes published two papers on the subject in 1957:

He acknowledged that Statistical Mechanics was not a physical theory,

But went further and claimed that it need not be: statistical inference allows physically useful properties of systems, such as mean energy and mean square deviation, to be derived

## Is this true of **entropy**?

Statistical mechanics agrees with thermodynamics.

If the increase in thermodynamic entropy in an irreversible adiabatic process has no physical basis in energy, what does this mean for the statistical entropy?

If we derive a set of physically descriptive distributions and the entropy is different from that of statistical mechanics, what does that mean?

## Gibbs:

A small part of a larger system is canonically distributed.

$$Pd\tau = p_1 p_2 p_3 \dots p_n \cdot dv_1 dv_2 dv_3 \dots dv_n = p(v)^n d^n v$$

↑  
system probability.



Single particle  
Maxwellians.

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

This leads directly to the **Gamma distribution**

$$P(E).dE = \frac{\beta^\gamma}{\Gamma(\gamma)} e^{-\beta E} E^{\gamma-1} dE$$

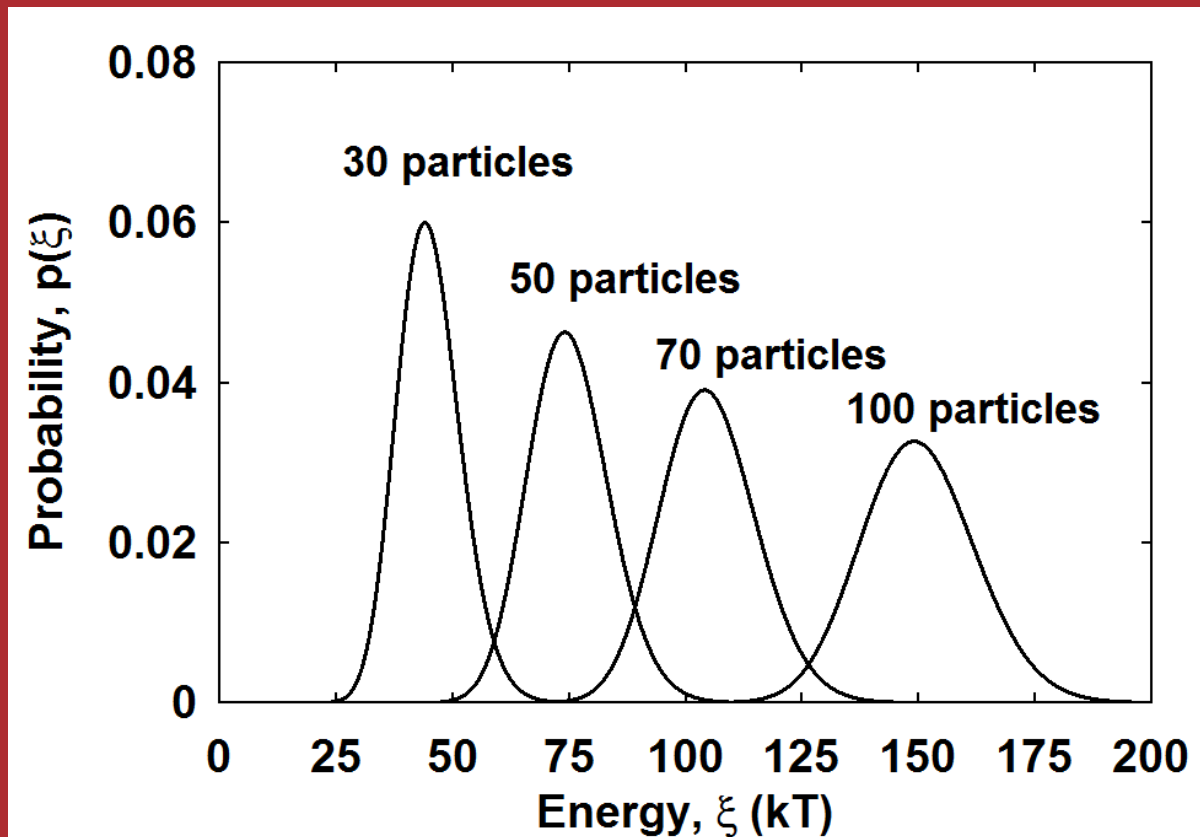
$$P(\xi).d\xi = \frac{\xi^{\gamma-1}}{\Gamma(\gamma)} e^{-\xi} .d\xi$$

$$\beta=(kT)^{-1}$$

$$\gamma=3n/2$$

$$\xi=\beta E$$

$$p(E_i) = \frac{1}{Z} e^{\frac{-E_i}{kT}}$$

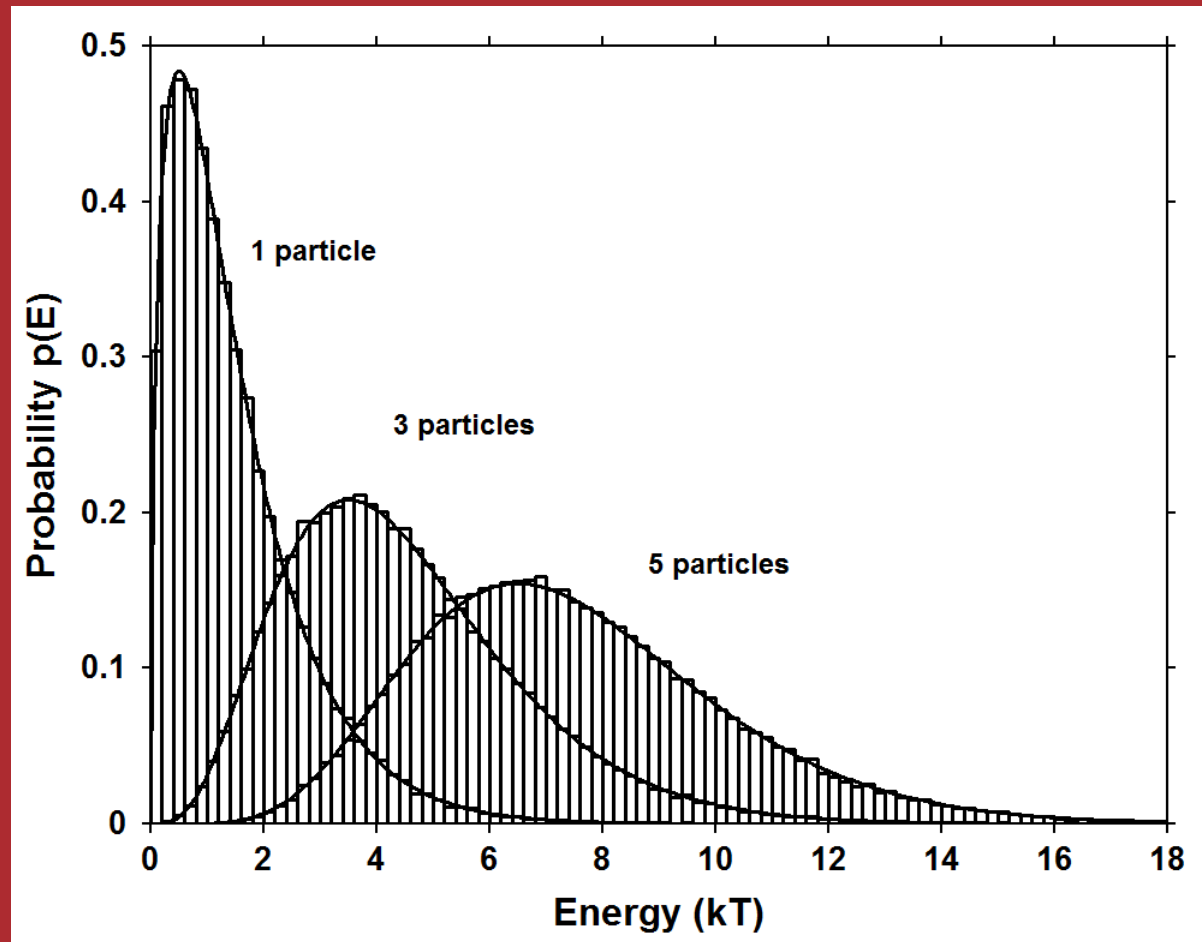




# Computer simulations of hard sphere fluid confirm the Gamma distribution

Histograms:  $10^5$  samples.  
solid lines: Gamma distribution

400 particles in total.

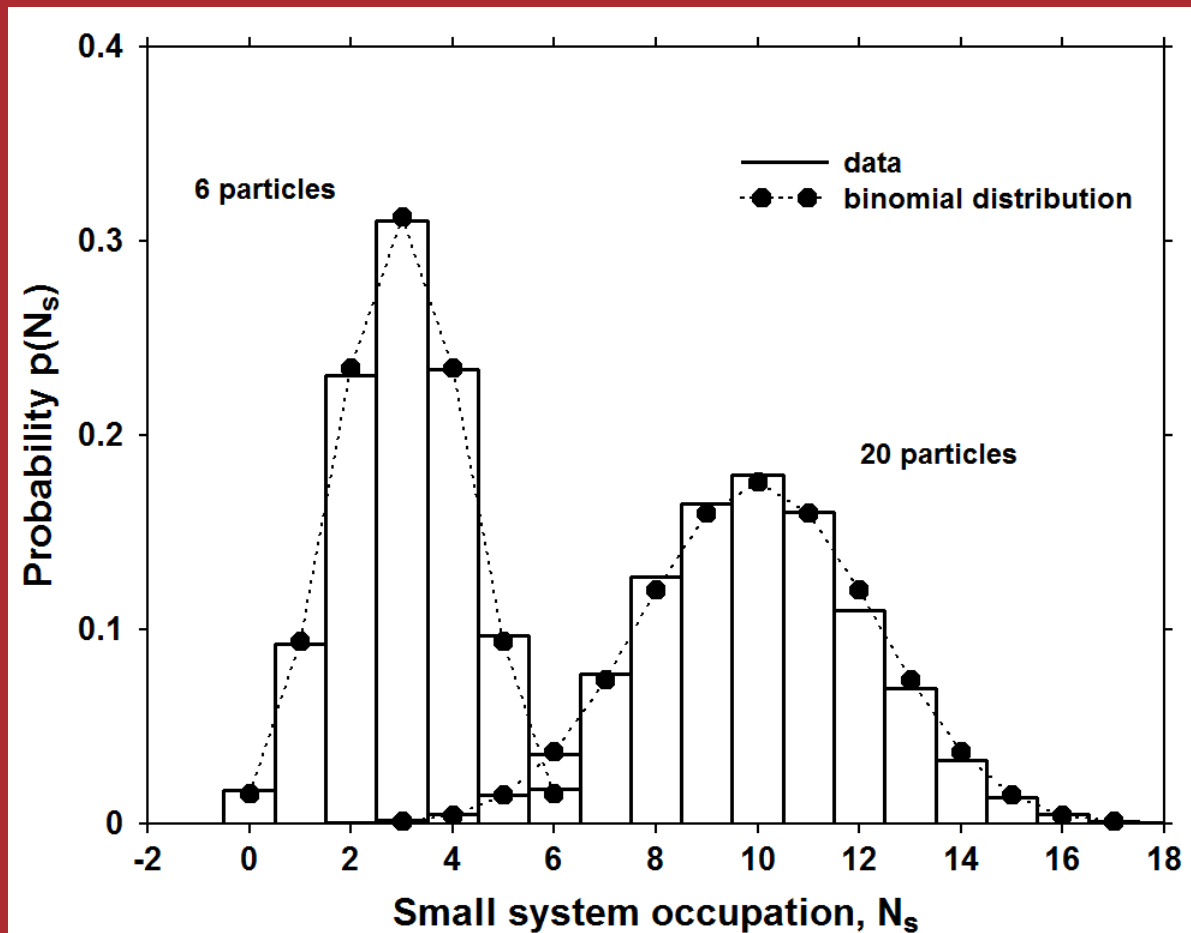


## Extension to **open systems**:

Insert permeable partition – a series of fixed spheres dividing the chamber, concentrate on one side only.

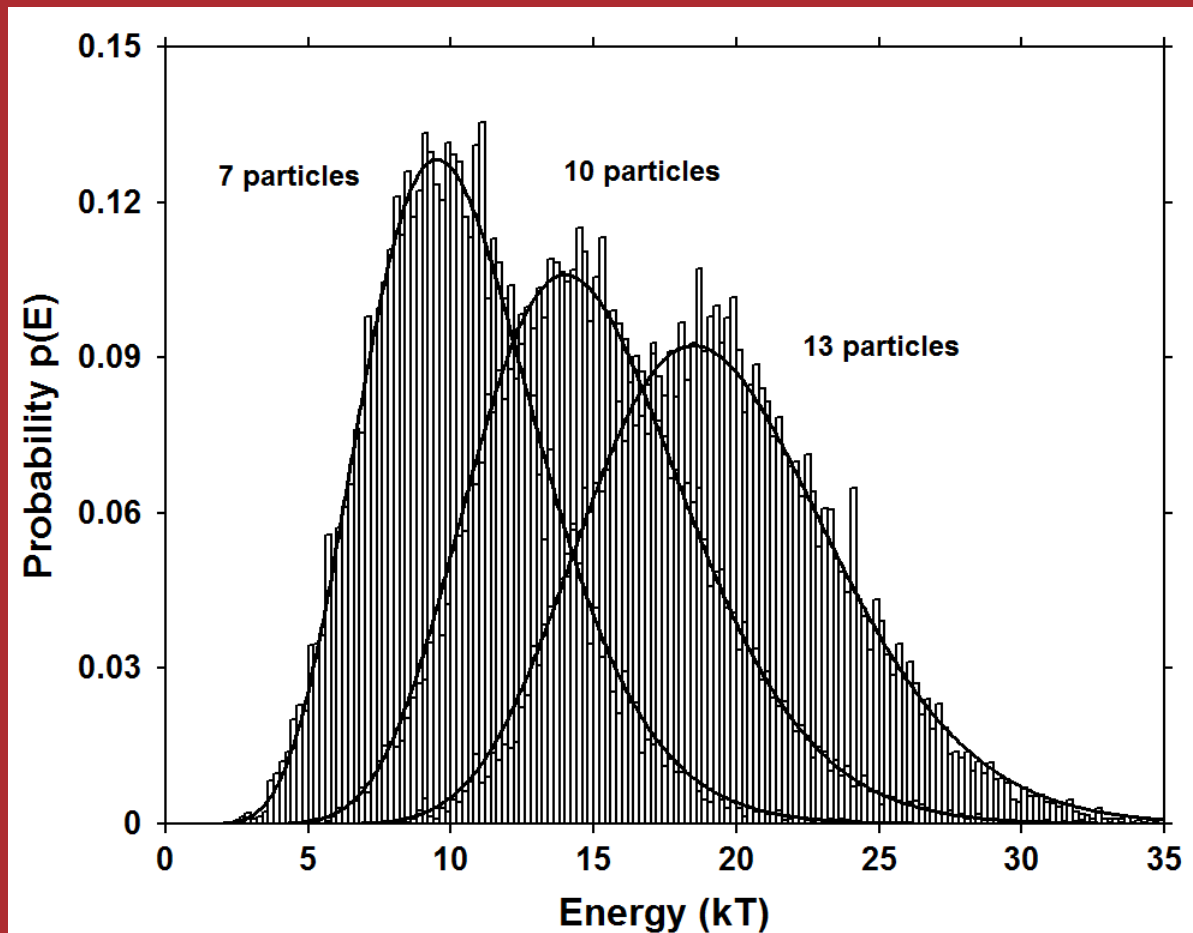
Look at a small part ( $n=6$ ,  $n=20$ ) of a larger system – 400 particles.

System occupancy – equal volumes



The energy distributions for three of the occupation numbers (7, 10 and 13) of the small system of 20 particles

solid lines: Gamma distribution

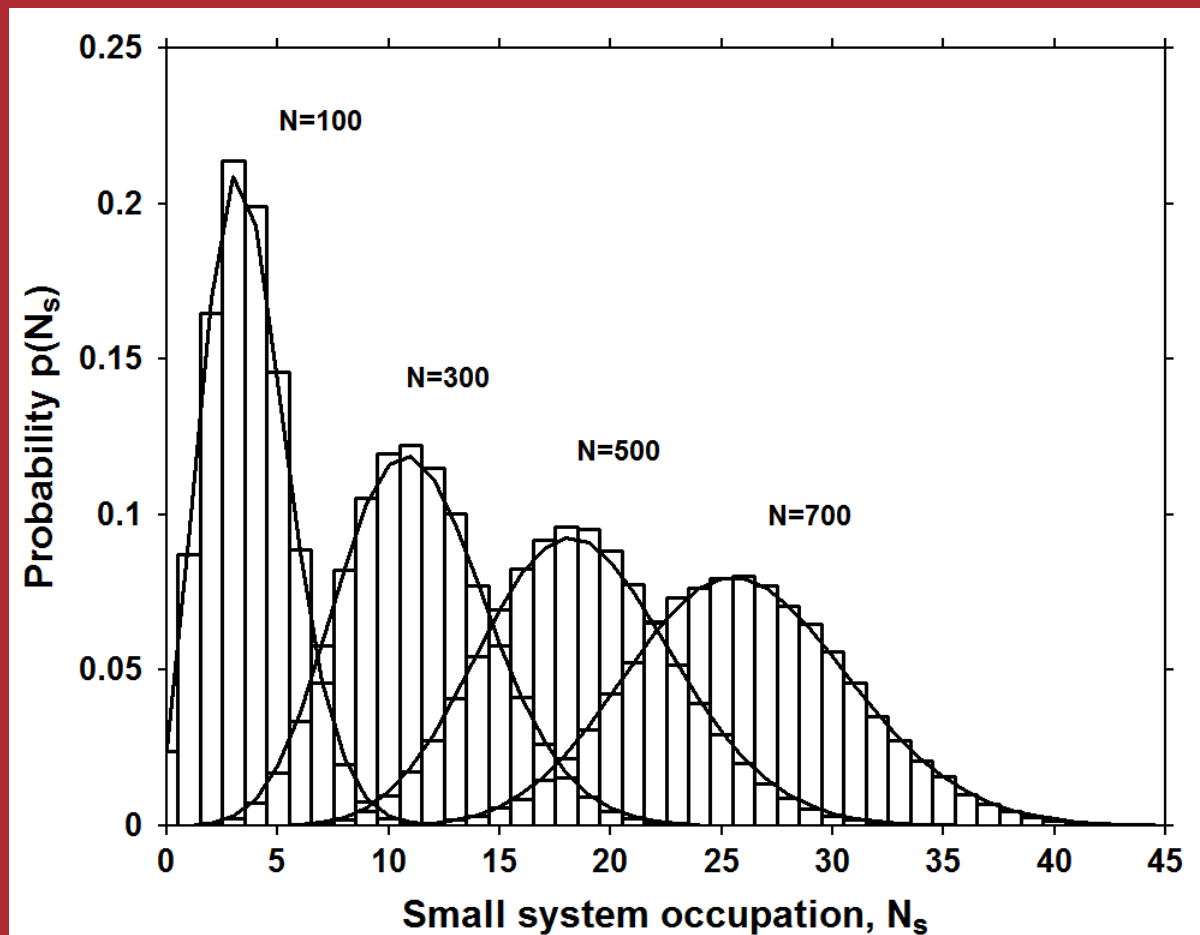


For very large ratios of volumes the larger system becomes both a thermal and particle reservoir – the small system occupancy is given by the Poisson distribution

Ratio of volumes 24:1

Total numbers of particles:

100, 300, 500, 700



The distribution of energy states in the smaller system as again given by the weighted sum of gamma distributions

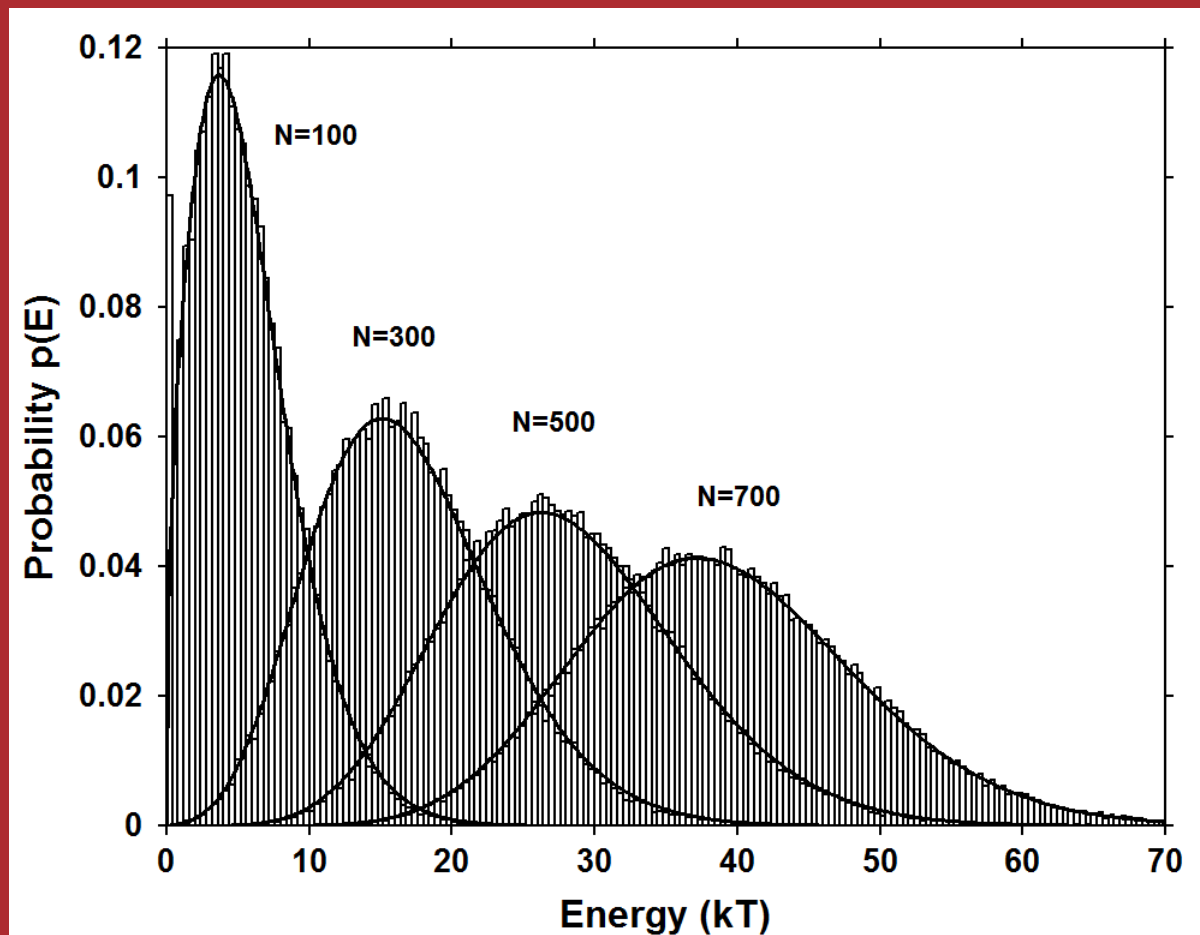
$$p(n, E_{n,i}) = p(n) \cdot p(E_{n,i})$$

$$p(E_i) = \sum_n p(n, E_{n,i})$$

Ratio of volumes 24:1

Total numbers of particles:

100, 300, 500, 700



**Entropy:** Is the information entropy the same as thermodynamic entropy?

Which variable? Energy or phase?

**Energy**

$$P(\xi).d\xi = \frac{\xi^{\gamma-1}}{\Gamma(\gamma)} e^{-\xi} .d\xi$$



$$H(\xi) = -\ln\Gamma(\gamma) + (\gamma - 1)\overline{\ln \xi} - \overline{\xi}$$

$$P(E).dE = \frac{\beta^\gamma}{\Gamma(\gamma)} e^{-\beta E} E^{\gamma-1} dE$$



$$H(E) = H(\xi) + \ln \beta$$

# Phase

$$P(\tau)d\tau = p_1 p_2 p_3 \dots p_n \cdot dv_1 dv_2 dv_3 \dots dv_n \frac{1}{V^n} d^n V = \frac{1}{V^n} d^n V \cdot p(v)^n d^n v$$



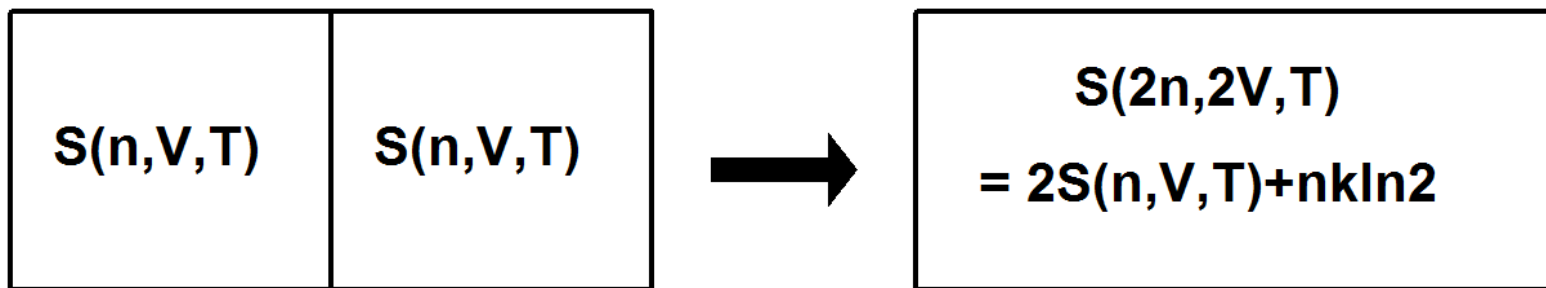
$$H(\tau) = \frac{3}{2} n \ln T + n \ln V + \dots$$

For physically descriptive statistical distributions the entropy taken over the distribution of energy states differs from energy taken over the phase space probability.

Only the latter agrees with thermodynamics as we know it.

$$S = \int \frac{dQ}{T} = \int \left( \frac{dU}{T} + \frac{p}{T} dV \right) = \frac{3}{2} nk \ln T + nk \ln V$$

But, Gibbs' paradox!





## Entropy in open systems

$$p(n, \tau_{n,i}) = p(n) \cdot p(\tau_{n,i})$$

$$S(n, \tau) = -k_B \left[ H(n) + \sum_n p(n) H(\tau) \right]$$

$$S = \frac{3}{2} \bar{n} k \ln T + \bar{n} k \ln V + k H(n) + \dots$$

$$H(n) \approx -\frac{1}{2} \ln \bar{n}$$

$H(n)$  is clearly non-thermodynamic

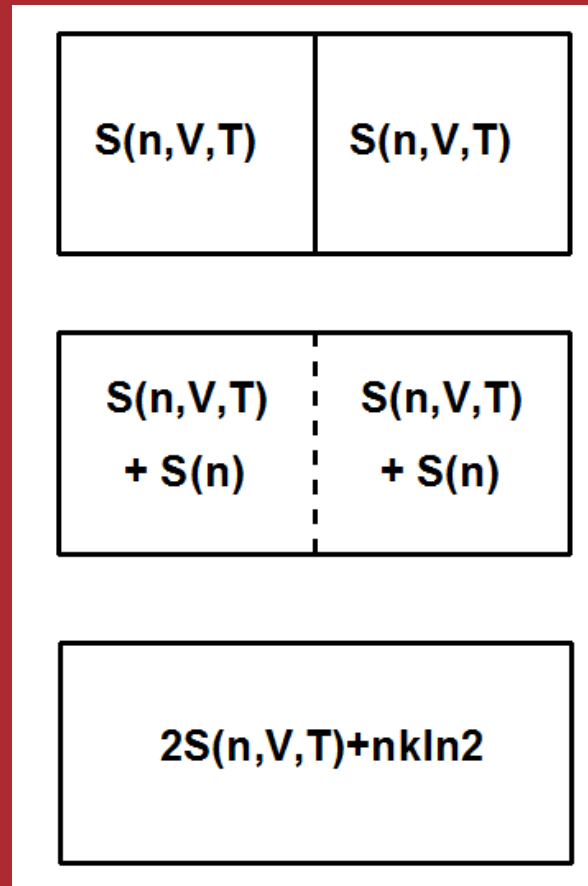
# What about H(V)?

Planck: correct for over counting by dividing partition function by N!

Information theory: doesn't deal with states but with probability

$$p(V).dV = \frac{1}{V} dV$$

is normalized



Remove constraints:  
entropy increases



**Thermodynamic and information entropies would appear to be different!**

Statistical entropy should be regarded as an aspect of probability theory and taught as such.

Maximising the entropy is equivalent to finding the most probable distribution!

# Conclusions

1. Doubts over the concept of the entropy of a body,
2. Gibbs' statistical mechanics is not a physical theory and attempts to relate it to physical phenomena through entropy fluctuations are flawed.
3. Physically representative probability distributions in the classical ideal gas differentiate between energy and phase.
4. Information entropy contains non-thermodynamic components:  $H(n)$  and possibly  $H(V)$ .
5. Thermodynamic and information entropies would appear to be different.
6. Statistical entropy is a very useful property for characterizing uncertainty and for finding the most probable distribution.

**Fin.**

**Thank you  
for your time.**

# Addenda

## Gibbs' statistical mechanics

Presented the canonical ensemble in 1902.

Not intended to represent a physical system.

“I have found it convenient, instead of considering one system of material particles, to consider a large number of systems similar to each other in all respects except in the initial circumstances of the motion, which are supposed to vary from system to system, the total energy being the same in all. In the statistical investigation of the motion, we confine our attention to the number of these systems which at a given time are in a phase such that the variables which define it lie within given limits.”

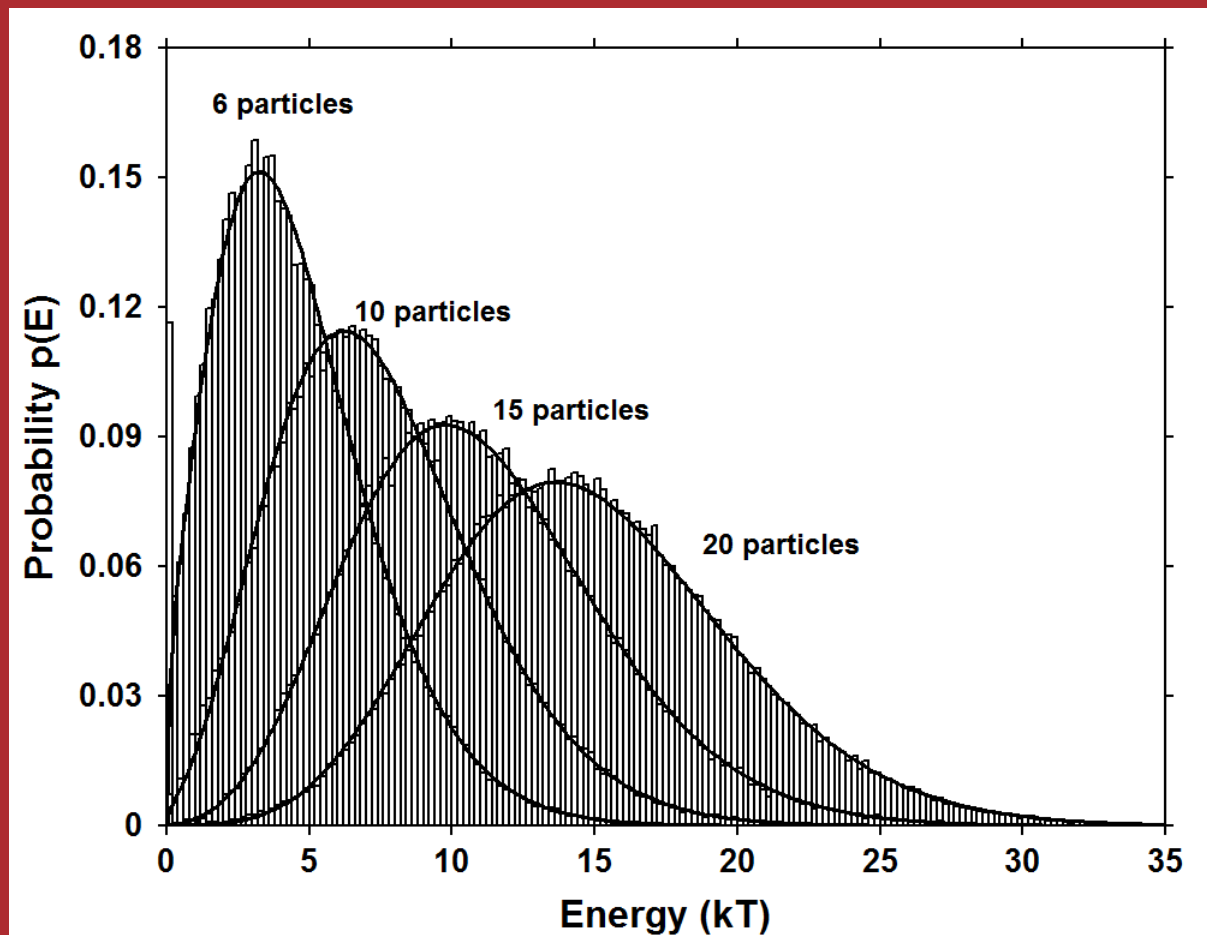
J.C. Maxwell, On Boltzmann's theorem on the average distribution of energy in a system of material points, Cambridge Philosophical Society's Transactions, Vol. XII., 1876

The distribution of energy states for four small systems; 6, 10, 15 and 20 particles in 400, equal volumes

solid lines: weighted sum of Gamma distributions

$$p(n, E_{n,i}) = p(n) \cdot p(E_{n,i})$$

$$p(E_i) = \sum_n p(n, E_{n,i})$$



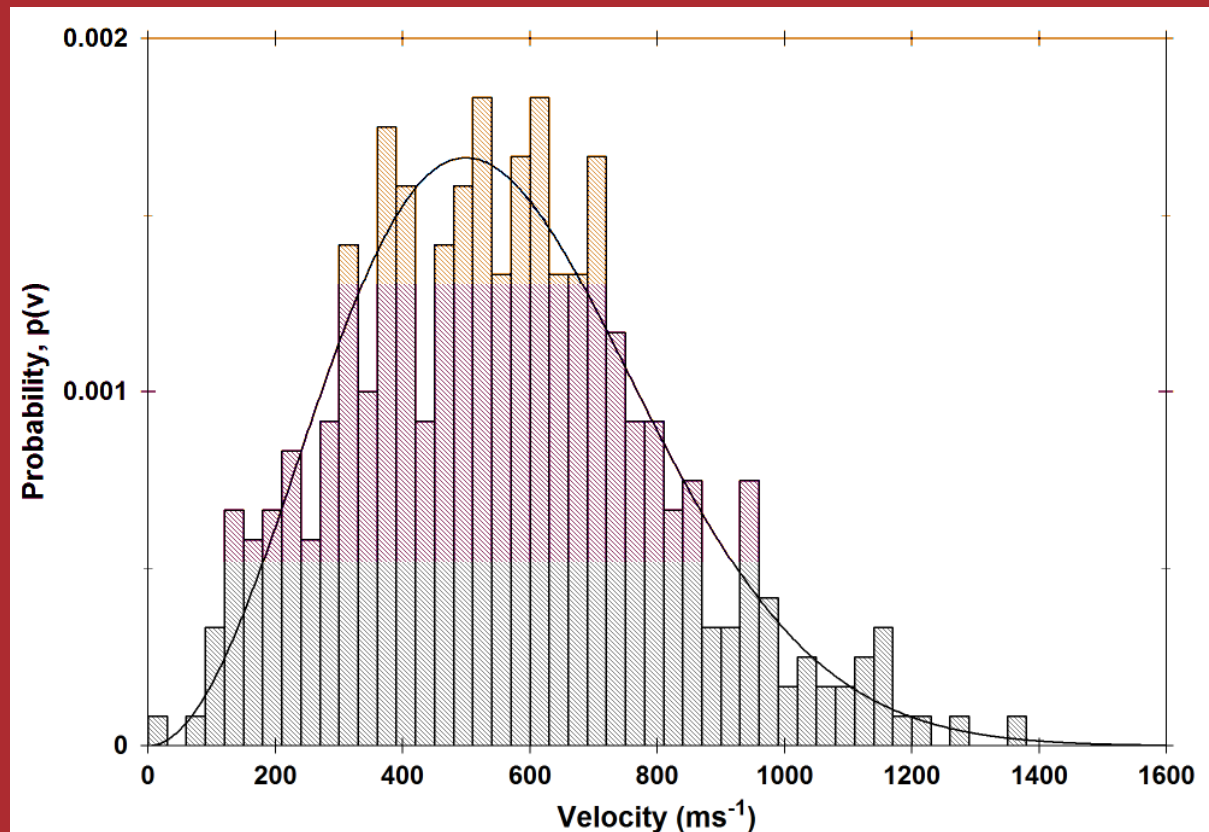


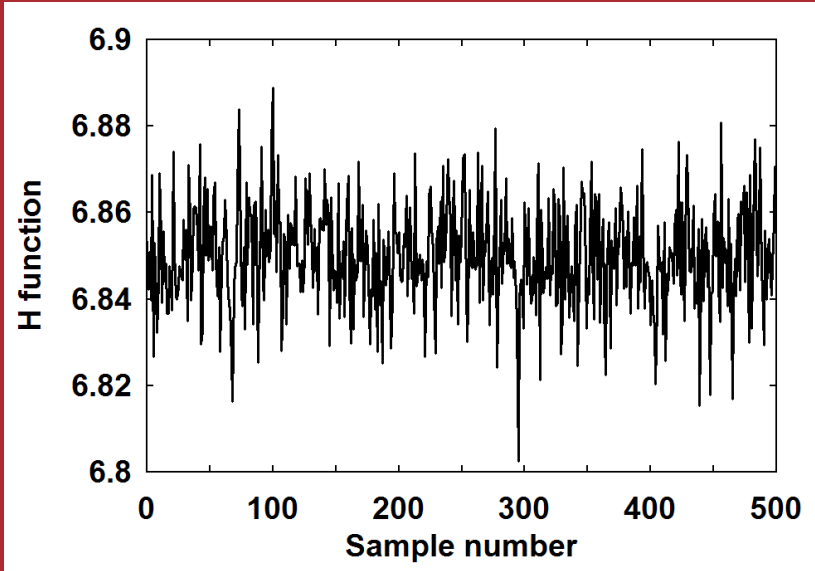
# 1. Fluctuations in energy

Entropy in IT represents uncertainty; it should not fluctuate with the state of the system.

The single-particle Gamma distribution shows that the velocity of a single particle is always governed by the Maxwellian.

Distribution of velocities across 300 particles (intervals of 30  $\text{ms}^{-1}$ )





Fluctuations in the H-function for a system of 2000 particles

Mean H-function for systems of different sizes

