

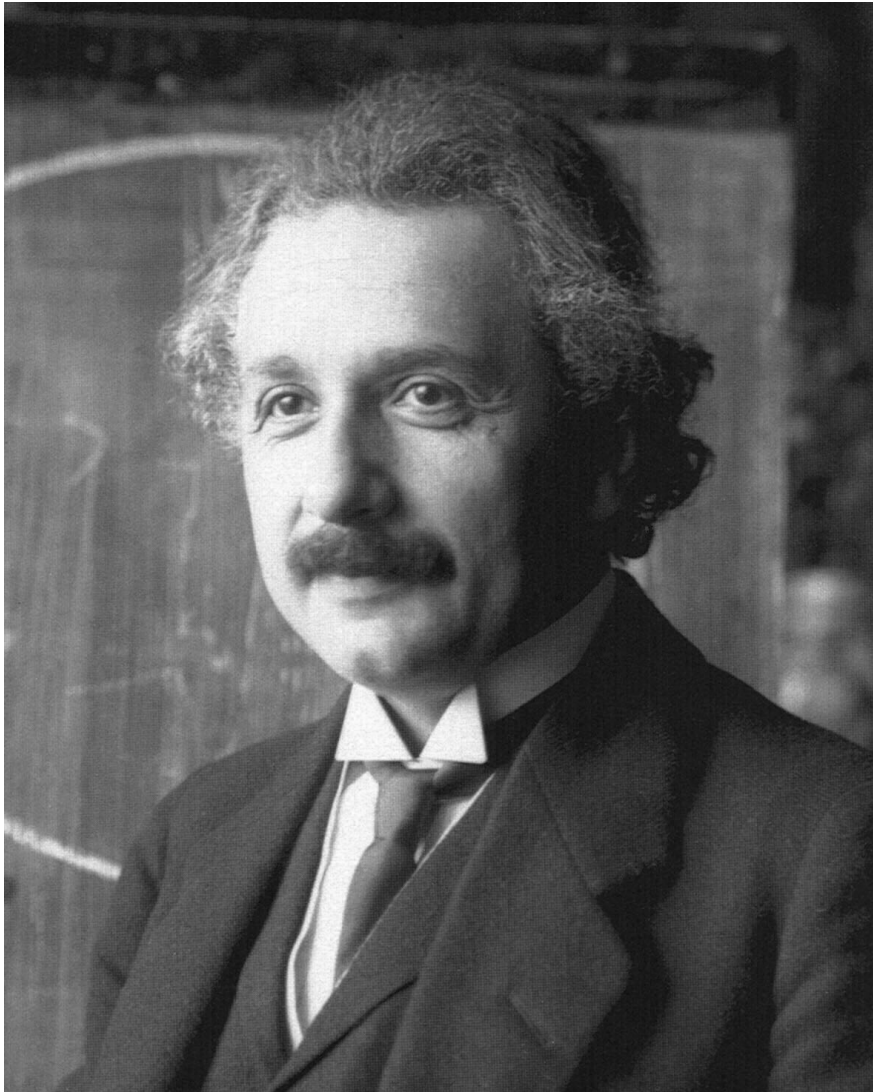
STATISTICAL MOLECULAR THERMODYNAMICS

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Video 3.1

Boltzmann Probability

THERMODYNAMICS: HISTORY



“A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore, the deep impression which *classical thermodynamics* made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.”

A. Einstein

THERMODYNAMICS: HISTORY

Thermodynamics is the study of energy and its transformations.

Considerable progress was made on thermodynamics *before* the atomic theory of matter was generally accepted. **Classical thermodynamics** encompasses a very powerful set of laws (we'll see many later), but they offer zero molecular insight.

Concomitant with the development of an atomic and molecular understanding of matter, **statistical thermodynamics** was developed to connect *microscopic* properties to the already well established *macroscopic* behavior of substances.

Most simply put, **statistical thermodynamics** relates the **averages of molecular properties** to bulk **thermodynamic properties**, like pressure, temperature, enthalpy, etc.

LUDWIG BOLTZMANN, 1844-1906



The Boltzmann equation (1877) of statistical thermodynamics:

$$S = k_B \ln W$$

Entropy (S) and **Wahrscheinlichkeit** (W ; number of microstates, disorder, degeneracy, likelihood/probability) are related by the Boltzmann constant

$$k_B$$

$$k_B = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$$

$$R = k_B N_A$$

THE VERY LARGE WATER COOLER (ENSEMBLE AT FIXED TEMPERATURE T)

There are about 10^{25} molecules (N) in a 330 mL volume (V) with the molecules interacting with one another in each bottle.

We know from quantum mechanics that there is an enormous set of allowed macroscopic energies. This set of energies will be a function of both N and V :

$$\{E_i(N, V)\}$$

Allowed set of energies

The Key Question

What is the probability that *your* water will be in state i with energy E_i ?



NUMBERS OF STATES

We will use a_i to indicate the number of bottles having energy $E_i(N, V)$ for the (fixed) number of particles N and volume V

The *ratio* of the number of bottles in “states” j and k will be given by some function of energy f such that:

$$\frac{a_j}{a_k} = f(E_j, E_k)$$

Important: this ratio should *not* depend on the (arbitrary) choice of zero for E , so we have:

$$\frac{a_j}{a_k} = f(E_j - E_k)$$

NUMBERS OF STATES

$$\frac{a_j}{a_k} = f(E_j - E_k)$$

Consider another system having energy E_l . The ratio of a_j to a_l and of a_k to a_l must be, respectively:

$$\frac{a_j}{a_l} = f(E_j - E_l) \quad \frac{a_k}{a_l} = f(E_k - E_l)$$

In addition,

$$\frac{a_j}{a_l} = \frac{a_j}{a_k} \cdot \frac{a_k}{a_l} = f(E_j - E_k) f(E_k - E_l)$$

So,

$$f(E_j - E_l) = f(E_j - E_k) f(E_k - E_l)$$

NUMBERS OF STATES

$$f(\underbrace{E_j - E_l}_{x+y}) = f(\underbrace{E_j - E_k}_x) f(\underbrace{E_k - E_l}_y)$$

The exponential is the function that has the property:

$$f(x + y) = f(x)f(y)$$

This implies that our original number of states for a given energy E should be determined from:

$$a_i = C e^{-\beta E_i}$$

where C and β are arbitrary positive constants yet to be determined (β must be positive or our water cooler would need to be infinitely large; in addition, note that energy must be bounded from below for the same reason)