

STATISTICAL MOLECULAR THERMODYNAMICS

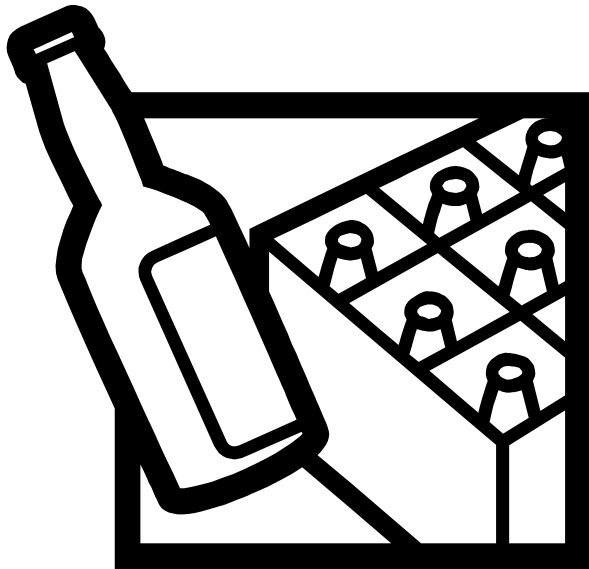
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Video 3.3

Ideal Gas Internal Energy

FUNDAMENTAL POSTULATE OF STATISTICAL THERMODYNAMICS

The observed energy of a given system corresponds to the average energy over all possible states of the ensemble each weighted according to its respective probability



$$\langle E \rangle = \sum_j p_j E_j = \sum_j \frac{E_j(N, V) e^{-\beta E_j(N, V)}}{Q(N, V, \beta)}$$

RELATION OF E AND Q

$$Q(N, V, \beta) = \sum_j e^{-\beta E_j(N, V)}$$

$$\langle E \rangle = \sum_j \frac{E_j(N, V) e^{-\beta E_j(N, V)}}{Q(N, V, \beta)}$$

Some elementary differential calculus:

$$\frac{\partial \ln Q}{\partial Q} = \frac{1}{Q} \quad \left(\frac{\partial Q}{\partial \beta} \right)_{N, V} = - \sum_j E_j(N, V) e^{-\beta E_j(N, V)}$$

So,

$$-\left(\frac{\partial \ln Q}{\partial \beta} \right)_{N, V} = - \left(\frac{\partial \ln Q}{\partial Q} \right) \left(\frac{\partial Q}{\partial \beta} \right)_{N, V} = \frac{1}{Q} \sum_j E_j(N, V) e^{-\beta E_j(N, V)} = \langle E \rangle$$

RELATION OF E AND Q

$$Q(N, V, \beta) = \sum_j e^{-\beta E_j(N, V)} \quad \langle E \rangle = \sum_j \frac{E_j(N, V) e^{-\beta E_j(N, V)}}{Q(N, V, \beta)}$$
$$\langle E \rangle = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N, V}$$

Or, if more convenient to work with T instead of β

$$\beta = \frac{1}{k_B T} \quad \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V} = \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N, V} \left(\frac{\partial \beta}{\partial T} \right)_{N, V} = (-\langle E \rangle) \left(-\frac{1}{k_B T^2} \right)$$

which rearranges to:

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

PRACTICAL UTILITY OF Q

We have proven that statistical thermodynamics permits calculation of macroscopic (thermodynamic) properties (e.g., energy) for a large collection of particles (e.g., molecules) from the partition function Q . But, how do we get the partition function? A brobdingnagian task...

The “simplest” example: a monatomic *ideal* gas (e.g., He). In that case, Q can be written as:

$$Q(N, V, \beta) = \frac{[q(V, \beta)]^N}{N!}$$

q : partition function for 1 atom
 m : mass of atom
 h : Planck's constant

$$q(V, \beta) = \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} V$$

Derivations soon



SOME CALCULUS

Given: $Q(N, V, \beta) = \frac{[q(V, \beta)]^N}{N!}$ $q(V, \beta) = \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} V$

Then, $\ln Q = N \ln q - \ln N!$

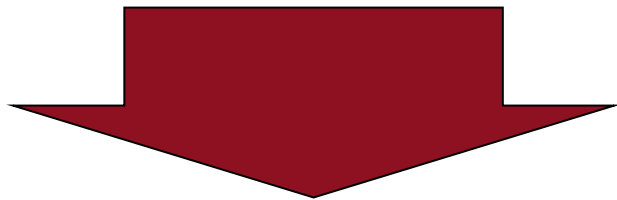
$$= \frac{3}{2} N (\ln 2\pi m - \ln h^2 - \ln \beta) + N \ln V - \ln N!$$

And, $-\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N, V} = \frac{3}{2} N \beta^{-1} = \frac{3}{2} N k_B T = \langle E \rangle$

pretty simple!

MONATOMIC IDEAL GAS REDUX

$$\langle E \rangle = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V}$$



$$\langle E \rangle = \frac{3}{2} N k_B T$$

From the kinetic theory of gases and from experiment, we know that the molar internal energy (\bar{U}) of a monoatomic ideal gas is:

$$\bar{U} = \frac{3}{2} RT$$

↙ *molar quantity
(i.e., per mole)*

This result demonstrates the power of statistical thermodynamics. From *microscopic* properties, we can calculate a *macroscopic quantity* that can be measured. It also establishes that Boltzmann's constant is equal to the universal gas constant R divided by Avogadro's number N_A

$$U = \langle E \rangle$$