Ludwig Boltzmann

Boltzmann is well-known as a chemical theorist – he worked on topics ranging from the kinetic theory of gases to the development of statistical thermodynamics… at a time when the atomic nature of matter was not understood or accepted!

His most famous equation, $S = k_B \ln W$, is printed on his tombstone and is a key expression to understanding entropy in terms of statistical thermodynamics. However, the equation and Boltzmann’s work in general was so highly criticized that he committed suicide without ever knowing the impact he had on modern chemistry.

$k_B = 1.38 \times 10^{-23}\ \mathrm{J{\cdot}K^{-1}}$ or $0.695\ \mathrm{cm^{-1}{\cdot}K^{-1}}$ $\qquad k_B N_A = R$

What is statistical thermodynamics?

- A way to connect the microscopic and macroscopic
- In principle, if enough information about the molecules in a system are known, the behavior of the system could be calculated from QM
- Statistical mechanics overcomes this impossible problem by predicting the most probable behavior of a large collection (ensemble) of molecules
- Summary: In statistical thermodynamics, the averages of molecular properties are related to thermodynamic properties (such as pressure and temperature) of macroscopic systems.

Review from QM Slides

1) Energy states for molecules are quantized.
2) Solve Schrödinger equation to find allowed states.
3) Given some T, how are these states populated?

Boltzmann Distribution

$$p_j = \frac{e^{-E_j/k_BT}}{\sum_i e^{-E_i/k_BT}}$$

Probability that a randomly chosen system will be in state j with E_j

Partition function

How does temperature affect the population of states?

What is p_j if E_j is big?

Consider a 330 mL hot chocolate

There are about 10^{24} molecules (N) in this volume (V) and we know that they all interact with each other.

But there must be a set of allowed macroscopic energies that come from the allowed electronic, vibrational, rotational, and translational energies of the individual molecules (recall QM?!). This set of energies will be a function of N and V:

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

What is the probability that *your* hot chocolate will be in state j with energy E_j?

Consider a tray of 10^6 hot chocolates!

The tray of hot chocolates is kept in thermal equilibrium with a heat reservoir. Each of the hot chocolates has the same N, V, and T. However, they can be in different quantum states. This collection of hot chocolates is an ensemble.

Total # of hot chocolates = A

# of hot chocolates in state j (with E_j) = a_j

We want to know # of hot chocolates in each state! So what is the form of a_j?

$$a_j = Ce^{-\beta E_j}$$

Now… what are C and β?

C, β, and Q …

To find C, sum both sides of equation:

$$\sum_j a_j = C \sum_j e^{-\beta E_j} = ?$$

$$\boldsymbol{C = ?}$$

$$\frac{a_j}{A} = p_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

p_j is the probability that a randomly chosen hot chocolate will be in quantum state *j*

Let the denominator = *Q*

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

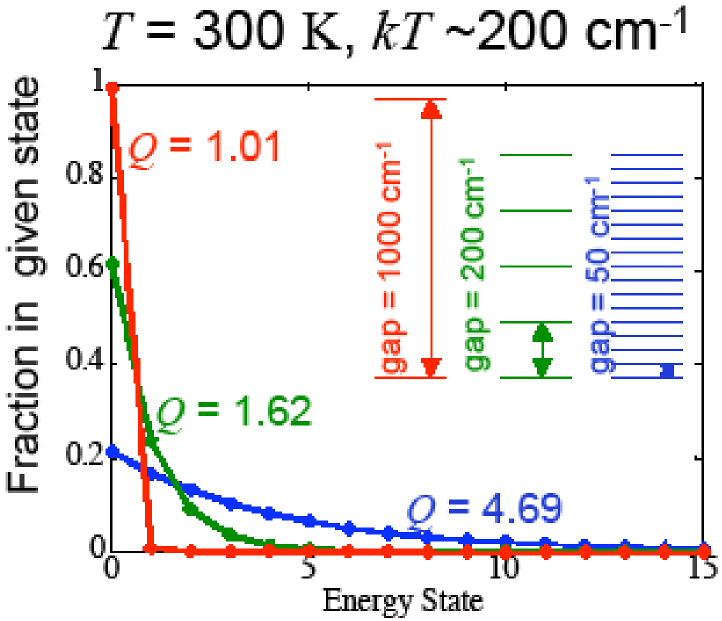
What is *Q* called?

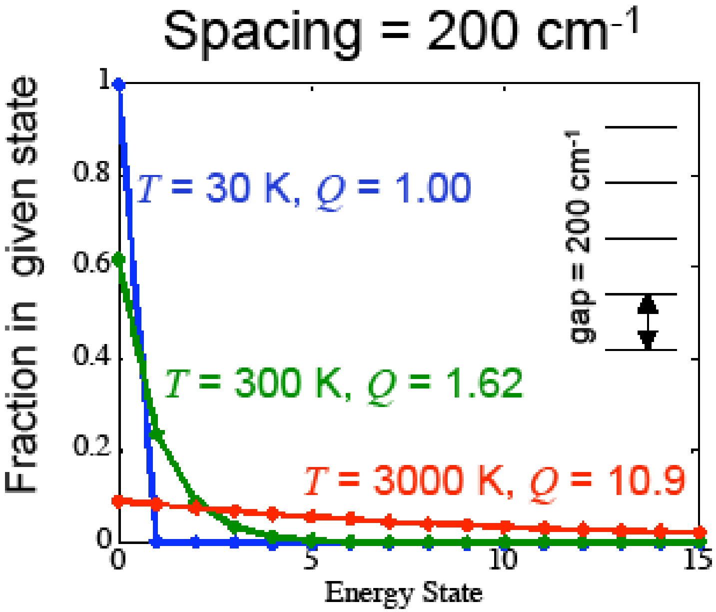
We will show later that:

$$\beta = \frac{1}{k_B T}$$

What is the partition function?

1. The denominator in the Boltzmann probability (i.e., the normalization constant).
2. A measure of the extent to which the particles are able to escape from the ground state (i.e., a measure of population in excited states).


T = 300 K, kT ~200 cm^{-1}


Spacing = 200 cm^{-1}

One more slide on *Q*!

One can express ***all*** **macroscopic properties** of a system in terms of *Q*!

Postulate – the averaged ensemble energy is the observed energy of a given system. That is:

$$\langle E\rangle = \underbrace{\sum_j p_j E_j}_{\text{See Math Ch B}} = \sum \frac{E_j(N,V)e^{-\beta E_j(N,V)}}{Q(N,V,\beta)}$$

In terms only of *Q* …

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

Ideal gas Law

The partition function, *Q*, for a monoatomic ideal gas can be written as:

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

where

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

q partition function for 1 atom
m mass of the atom
h Planck’s constant
N number of atoms

From this information about the partition function, we can calculate the macroscopic properties (e.g., energy) for an ensemble (e.g., a large collection of monoatomic gas molecules). The derivation of Q will be discussed soon…

Find <E> for an ideal gas…

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

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

Find ln(Q) and separate out the terms involving β

Differentiate with respect to β

From the kinetic theory of gases, we know the internal energy of a monoatomic ideal gas is:

$$U = 3/2\, nRT$$

$N = nN_A$ and $R = k_B N_A$

Other Macroscopic Properties

The result of U = <E> on the previous slide demonstrates the power of statistical thermodynamics. From *microscopic* properties, we can calculate any *macroscopic* quantity we want!

Other macroscopic quantities:

$$\overline{C}_V = \left(\frac{\partial \overline{U}}{\partial T}\right)_V = \left(\frac{\partial \langle \overline{E} \rangle}{\partial T}\right)_V$$

Heat capacity: the energy required to raise the temperature of a given amount of substance by 1K.

What is $\overline{C}_V$ for a monoatomic ideal gas?

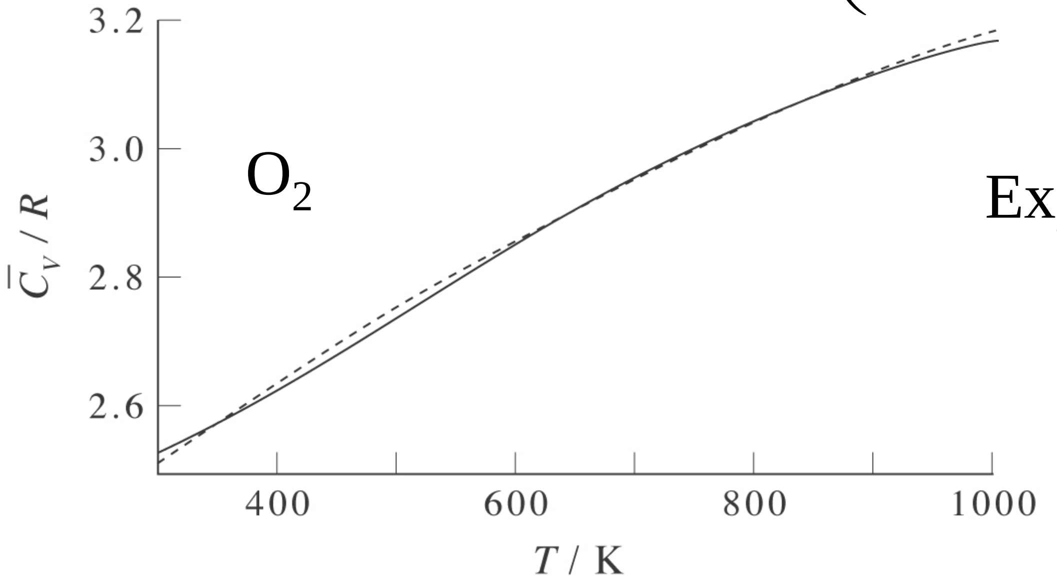
$$\langle P \rangle = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

Pressure

Heat capacity

From the partition function for a diatomic gas, you can derive the constant volume heat capacity…

$$\overline{C}_V = \frac{5}{2}R + R\left(\frac{h\upsilon}{k_B T}\right)^2 \frac{e^{\frac{-h\upsilon}{k_B T}}}{\left(1-e^{\frac{-h\upsilon}{k_B T}}\right)^2}$$



Experiment vs. Theory

<P> for Monoatomic Ideal Gas

$$\langle P \rangle = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta} \qquad Q(N,V,\beta) = \left(\frac{2\pi m}{h^2 \beta} \right)^{3N/2} \frac{V^N}{N!}$$

Find ln(Q) and separate out the terms involving V

Differentiate with respect to V

$$\langle \boldsymbol{P} \rangle = \boldsymbol{k_B T} \left(\frac{\partial \ln \boldsymbol{Q}}{\partial \boldsymbol{V}} \right)_{\boldsymbol{N},\beta} = ?$$

Obviously Q is important!!

The partition function plays a significant role in statistical thermodynamics. Q comes from an understanding of allowed energies of a given system and this comes from quantum mechanics (i.e., what states are allowed by the laws of QM).

Q as we have been using it, with N, V, and T fixed, refers to the partition function for the system and can be referred to as the **canonical partition function** and the ensemble (of hot chocolates) that we constructed is the **canonical ensemble**. There are other ensembles!!

Q is all we need to get macroscopic properties, but to do so for an arbitrary system, we need the eigenvalues for the N-body Schrodinger equation… no can do. But, we can get Q from “individual” molecular information!

Q in terms of q

Consider a system of *distinguishable, independent* particles…

The total energy of the system is:

$$E_l(N,V) = \varepsilon_i^a(V) + \varepsilon_j^b(V) + \varepsilon_k^c(V) + \ldots$$

The partition function becomes:

$$Q(N,V,T) = \sum_l e^{-\beta E_l} = \sum_{i,j,k\ldots} e^{-\beta(\varepsilon_i^a + \varepsilon_j^b + \varepsilon_k^c + \ldots)}$$

$$Q(N,V,T) = q_a(V,T)\, q_b(V,T)\, q_c(V,T) \ldots$$

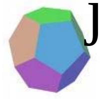
$$q(V,T) = \sum_i e^{-\beta \varepsilon_i}$$

Depends only on individual molecules/atoms!

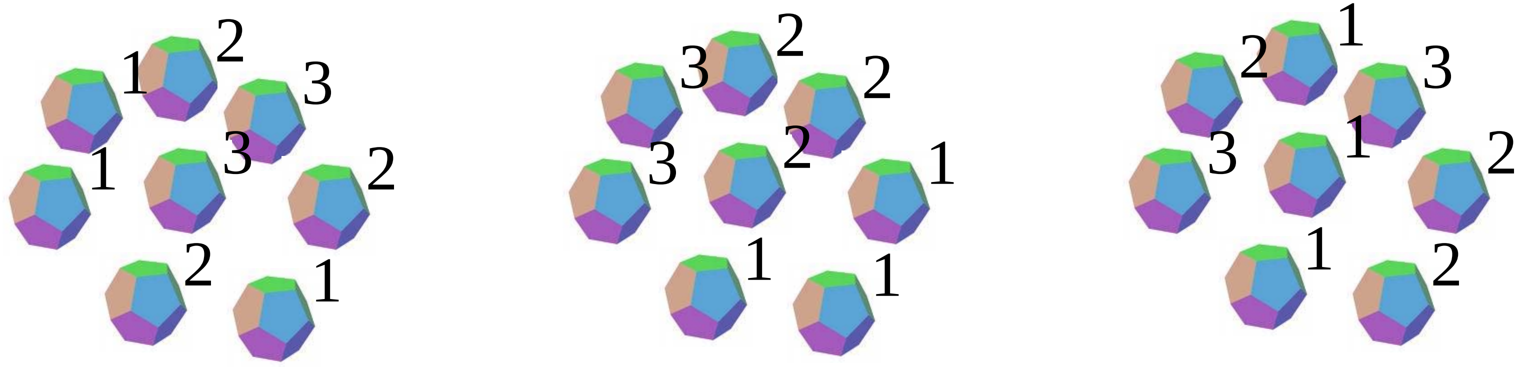
If all particles are identical: $Q(N,V,T) = [q(V,T)]^N$

Distinguishable? Get real…

$Q(N,V,T) = [q(V,T)]^N$ is a nice result, but not very useful. Atoms/molecules are usually *indistinguishable*.

Let  ^{j} be an atom with energy ε_j and only ε_1, ε_2, and ε_3 are allowed.

Consider the 3 situations below...



Each of these situations represent the same state and should be "counted" only once (i.e., since these states are indistinguishable but are the same, there is an "over-counting").

Now consider a *(not so)* special case

Consider a system in which no two atoms have the same energy. In that case, you can divide by $N!$ to account for over-counting.

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

How special is this case? … If the number of quantum states with energies less than $\sim k_B T$ is much greater than N, then odds are very good that no two particles will have the same energy.

Let me “translate” this concept

Remember translational energies vs k_BT (EX-QM5)?

Trans ~ $10^{-6} – 10^{-15}$ cm^{-1} k_BT ~ 200 cm^{-1} at 300 K

At room temperature, there are typically so many translational states accessible to a particle that the number of states is >> *N*. So $Q = q^N/N!$ holds.

Everybody randomly pick a lottery number.
Anybody have the same?

$$\frac{41!}{6!(41-6)!} = 4{,}496{,}388 \ \text{possibilities}$$

Boltzmann Statistics

The criterion that the number of states exceeds the number of particles is:

$$\frac{N}{V}\left(\frac{h^2}{8mk_BT}\right)^{\frac{3}{2}} << 1$$

Favors large m, high T, and low N/V.

A system where this is valid obeys *Boltzmann statistics*.

For a system obeying Boltzmann statistics, partition function is:

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

Boltzmann statistics

Which of these follow Boltzmann statistics?

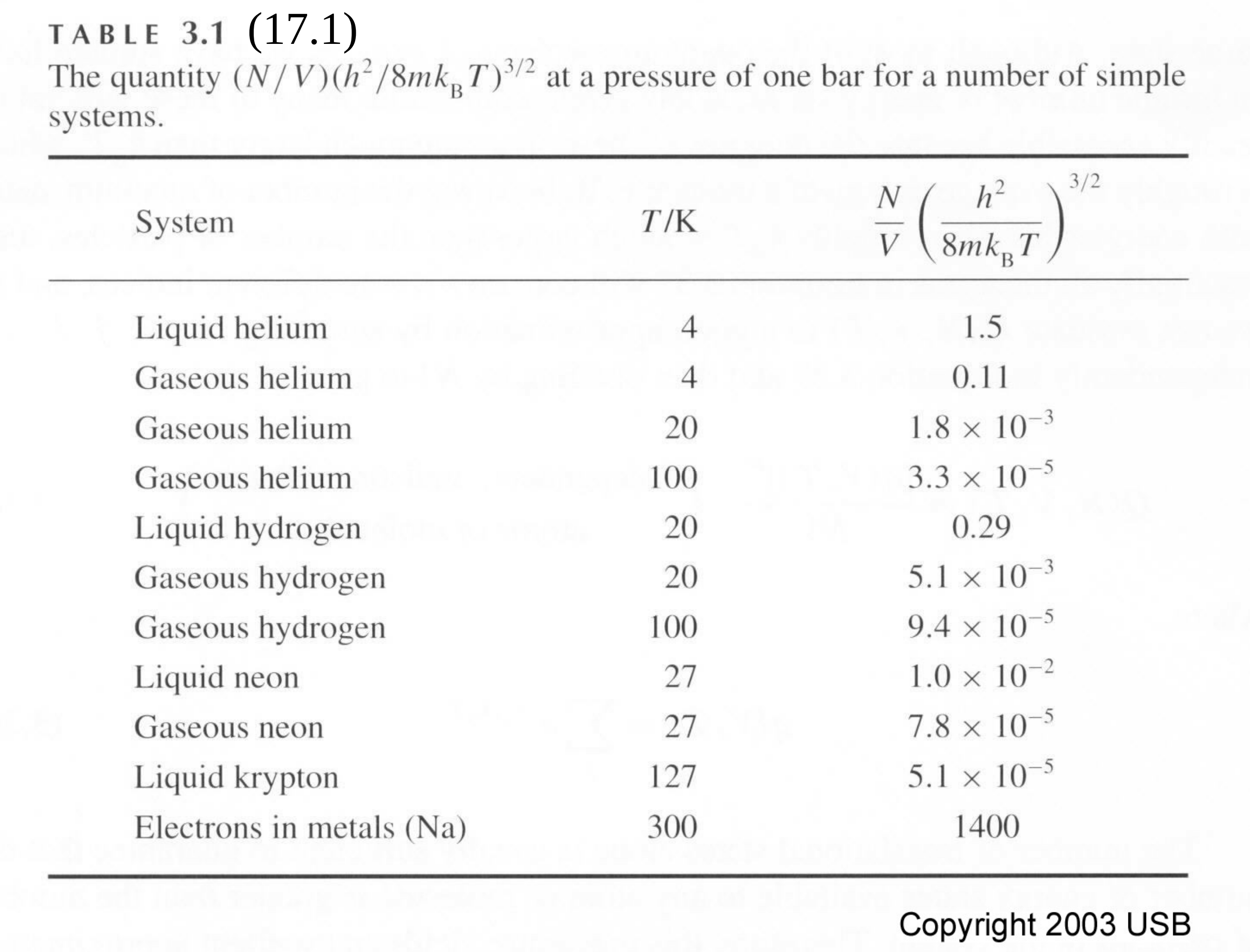


TABLE 3.1 (17.1)

The quantity $(N/V)(h^2/8mk_BT)^{3/2}$ at a pressure of one bar for a number of simple systems.

System	T/K	$\frac{N}{V}\left(\frac{h^2}{8mk_BT}\right)^{3/2}$
Liquid helium	4	1.5
Gaseous helium	4	0.11
Gaseous helium	20	1.8×10^{-3}
Gaseous helium	100	3.3×10^{-5}
Liquid hydrogen	20	0.29
Gaseous hydrogen	20	5.1×10^{-3}
Gaseous hydrogen	100	9.4×10^{-5}
Liquid neon	27	1.0×10^{-2}
Gaseous neon	27	7.8×10^{-5}
Liquid krypton	127	5.1×10^{-5}
Electrons in metals (Na)	300	1400

What characteristics cause some not to follow Boltzmann statistics?

Q vs q

Remember the probability of a member of an ensemble is in quantum state *j* is:

$$p_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

Similarly, the probability (π_j) that a molecule is in its *j*th molecular energy state is:

$$\pi_j = \frac{e^{-\beta \varepsilon_j}}{\sum_j e^{-\beta \varepsilon_j}}$$

We can further designate the probability as the probability of a molecule to be in a vibrational, rotational, translational or electronic state.

$$\pi_j = \frac{e^{-\beta \varepsilon_j^{vib}}}{\sum_j e^{-\beta \varepsilon_j^{vib}}}$$

$\langle \varepsilon \rangle$, Energy of a molecule

$$\left\langle \varepsilon^{vib} \right\rangle = \sum_j \pi_j^{vib} \varepsilon_j^{vib} = \sum_j \varepsilon_j^{vib} \frac{e^{-\beta \varepsilon_j^{vib}}}{\sum_j e^{-\beta \varepsilon_j^{vib}}} = \sum_j \varepsilon_j^{vib} \frac{e^{-\beta \varepsilon_j^{vib}}}{q_{vib}}$$

$$= -\frac{\partial \ln q_{vib}}{\partial \beta} = k_B T^2 \frac{\partial \ln q_{vib}}{\partial T}$$

$$\boxed{\begin{array}{ll} \left\langle \varepsilon^{rot} \right\rangle = k_B T^2 \dfrac{\partial \ln q_{rot}}{\partial T} & \left\langle \varepsilon^{elec} \right\rangle = k_B T^2 \dfrac{\partial \ln q_{elec}}{\partial T} \\ \left\langle \varepsilon^{trans} \right\rangle = k_B T^2 \dfrac{\partial \ln q_{trans}}{\partial T} & \left\langle \varepsilon^{vib} \right\rangle = k_B T^2 \dfrac{\partial \ln q_{vib}}{\partial T} \end{array}}$$

$$\left\langle \varepsilon_{tot} \right\rangle = \left\langle \varepsilon_{elec} \right\rangle + \left\langle \varepsilon_{vib} \right\rangle + \left\langle \varepsilon_{rot} \right\rangle + \left\langle \varepsilon_{trans} \right\rangle$$

Degeneracy

Partition functions have been written so far as a summation over *states*. States with the same energy we call *levels*. The levels have a *degeneracy*, *g*.

$$q(V,T) = \sum_{j,states} e^{-\beta\varepsilon_j}$$

Terms representing a degenerate level are repeated g_j times

$$q(V,T) = \sum_{j,levels} g_j e^{-\beta\varepsilon_j}$$

Terms representing a degenerate level are written once and multiplied by g_j

Writing the partition function as a summation over levels can be more convenient.

Summary: Key Concepts

We want to know the macroscopic thermodynamic properties of a system (e.g., P, C_v, U).

The ensemble average of one of these properties is equal to the observed (macroscopic) value (e.g., $\langle E \rangle = U$).

We can get all kinds of ensemble averages from the ensemble partition function Q.

We can get Q from molecular partition functions q and these come directly from quantum mechanics.

...And we are going to derive these next!!

Summary: Key Equations

Boltzmann Distribution

$$p_j = \frac{e^{-E_j/k_BT}}{\sum_i e^{-E_i/k_BT}}$$

Partition Function

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

For Boltzmann statistics…

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

Conversions…

$$\beta = \frac{1}{k_BT}$$

$N=nN_A$

$R=k_BN_A$

Macroscopic Properties

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

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

$$\overline{C}_V = \left(\frac{\partial \overline{U}}{\partial T}\right)_V = \left(\frac{\partial \langle \overline{E}\rangle}{\partial T}\right)_V$$

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