# Statistical Mechanics at Equilibrium, Part 2

**Last time**

Microstates

Configurations

Most probable configuration

**Today**

Temperature

Partition functions

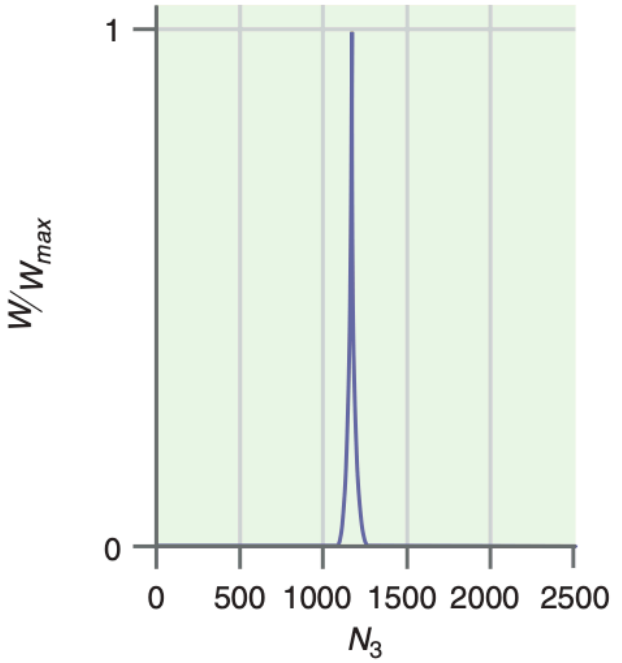
**Next time**

Energy

First law of thermodynamics

# Last time

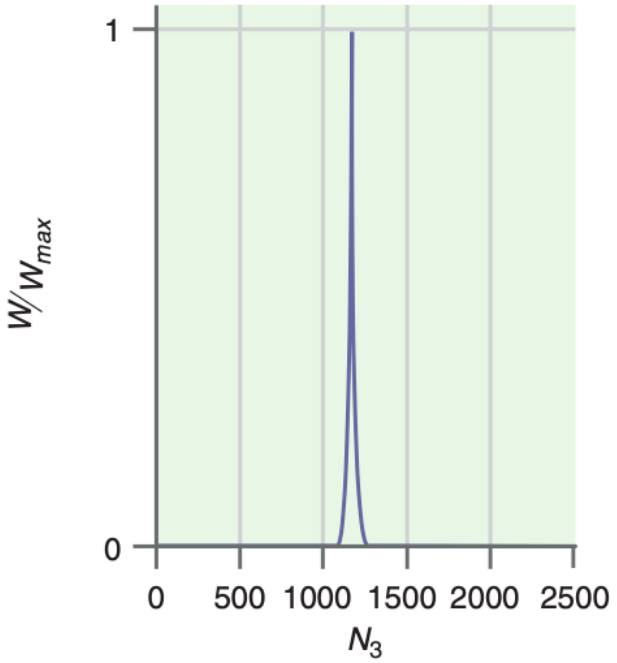
- Microstates vs. macrostates (configurations)
- All microstates are equally likely
- Weight of a configuration = number of corresponding microstates = number of ways to partition energy *E* among *N* molecules and get the same bulk properties
- In the thermodynamic limit, the most probable configuration dominates all others
- Equilibrium = dominant configuration
- Occupations and probabilities at equilibrium follow the Boltzmann distribution




$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

# Today

- What is β?
- What is the meaning of temperature?
- What is the meaning of the partition function?




$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

# Expectation values of observables

Instead of full probability distributions, we often want to know expectation values (or averages) of particular observables

$$\langle O \rangle = \sum_i p_i O_i$$

For example, the average energy of a molecule is

$$\langle \varepsilon \rangle = \sum_i p_i \varepsilon_i = \frac{\sum_i \varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}}$$

Similarly, the total energy of the *N* identical, independent molecules is

$$E = N \langle \varepsilon \rangle = \sum_i n_i \varepsilon_i = N \frac{\sum_i \varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}}$$

# What is β?

At equilibrium, an isolated system with constant *N* and *E* obeys the Boltzmann distribution

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

β is a Lagrange multiplier determined by the constraint of fixed total energy

$$E = \sum_i n_i\varepsilon_i = N\frac{\sum_i \varepsilon_i e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

Although this equation cannot be solved easily for β, β is a function of *N* and *E*

# β is the inverse temperature

We *define* the (absolute) temperature *T* so that

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

β has to have units of inverse energy

*k* is Boltzmann's constant, exactly 1.380649 × $10^{-23}$ J $K^{-1}$

$$\frac{n_i}{n_j} = e^{-\beta(\varepsilon_i - \varepsilon_j)}$$

The question is whether the temperature defined like this behaves as we'd expect

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# Absolute zero

The Boltzmann distribution shows us what is special about absolute zero

When $T = 0$,

$$\frac{\varepsilon_i - \varepsilon_0}{kT} = \infty$$

Therefore,

$$n_i = n_0 e^{-(\varepsilon_i - \varepsilon_0)/kT} = n_0 e^{-\infty} = 0 \quad \text{for } n_i \neq 0$$

$$n_0 = N$$

At absolute zero, all molecules are in the ground state

There cannot be a lower temperature, because there are no lower energies

# The temperature only exists at equilibrium

β (and, therefore, *T*) is a property of an equilibrium configuration.

It is a collective property of the system, and is defined for a system at equilibrium.

What if the configuration isn't an equilibrium configuration?

Can you still define a temperature for such a configuration?

No! There is no such thing as temperature for a system out of equilibrium.

# Zeroth law of thermodynamics

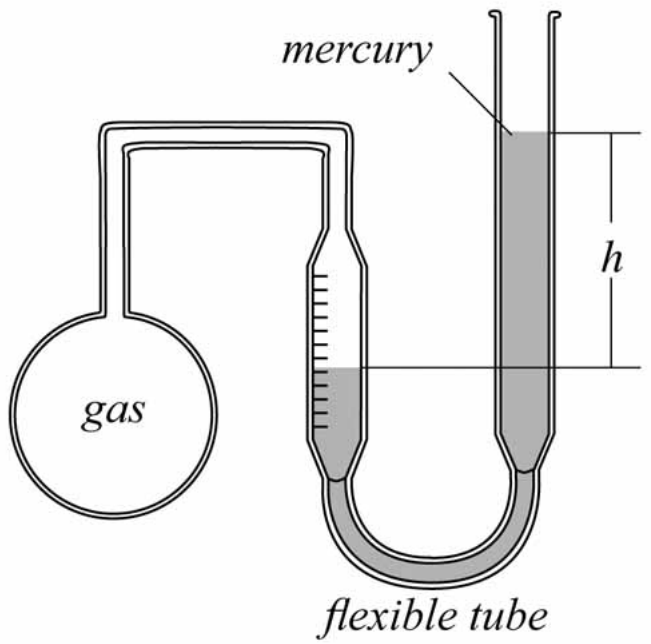
**If two systems are each in thermal equilibrium with a third, they are in thermal equilibrium with each other.**

In thermodynamics, the zeroth law essentially defines thermal equilibrium and ensures that there is a parameter (the temperature) that describes all systems in equilibrium with each other.

Later this week, we will see that the statistical temperature follows this rule, as well as the stronger statement that, in an isolated system, energy always flows from an area of higher temperature to an area of lower temperature.

# Zeroth law of thermodynamics

The zeroth law implies a probe system can be used to decide whether two systems will remain in equilibrium if brought into thermal contact with each other. These probes are called *thermometers*.




The absolute temperature *scale* is usually defined using the ideal-gas thermometer,

$$T = \frac{PV}{Nk}$$

# The partition function

The equilibrium probability distribution (Boltzmann distribution) tells us the probability of finding a molecule in state *i*:

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

The sum over all states in the denominator plays an important role and is called the *partition function*,

$$q = \sum_i e^{-\beta\varepsilon_i}$$

# Properties of the partition function

What physical interpretation can we make of *q*?

$$q = \sum_i e^{-\beta\varepsilon_i}$$

Each state contributes its occupation relative to the ground-state occupation:

$$e^{-\beta\varepsilon_i} = n_i/n_0$$

Therefore, *q* increases with the occupancy of excited states, i.e., with *T*

If $T \rightarrow 0$, then $q \rightarrow 1$, i.e. all molecules are in the ground state

If $T \rightarrow \infty$, then $q \rightarrow$ the number of molecular states

**The partition function is, *roughly*, the number of thermally accessible states per molecule.**



# Example

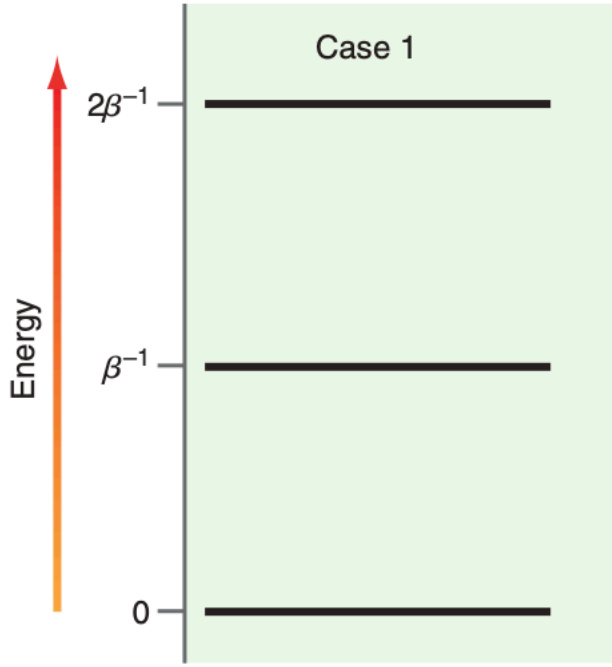
Consider a harmonic oscillator with $h\nu = \beta^{-1}$

$$\varepsilon_i = ih\nu = i\beta^{-1}$$

$$e^{-\beta\varepsilon_i} = e^{-i}$$

$$q = \sum_{i=0}^{\infty} e^{-i} = 1 + e^{-1} + e^{-2} + \ldots$$

$$= \frac{1}{1 - e^{-1}} = 1.58$$



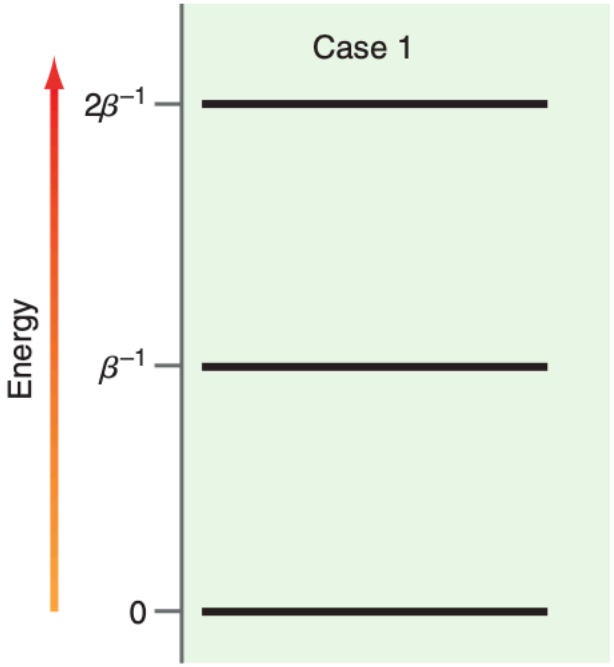
# Example

The probabilities of an oscillator occupying the first three levels are then:

$$p_0 = \frac{e^{-\beta\varepsilon_0}}{q} = \frac{e^{-0}}{1.58} = 0.633$$

$$p_1 = \frac{e^{-\beta\varepsilon_1}}{q} = \frac{e^{-1}}{1.58} = 0.233$$

$$p_2 = \frac{e^{-\beta\varepsilon_2}}{q} = \frac{e^{-2}}{1.58} = 0.086$$




Roughly 1.58 states are appreciably occupied

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# Example

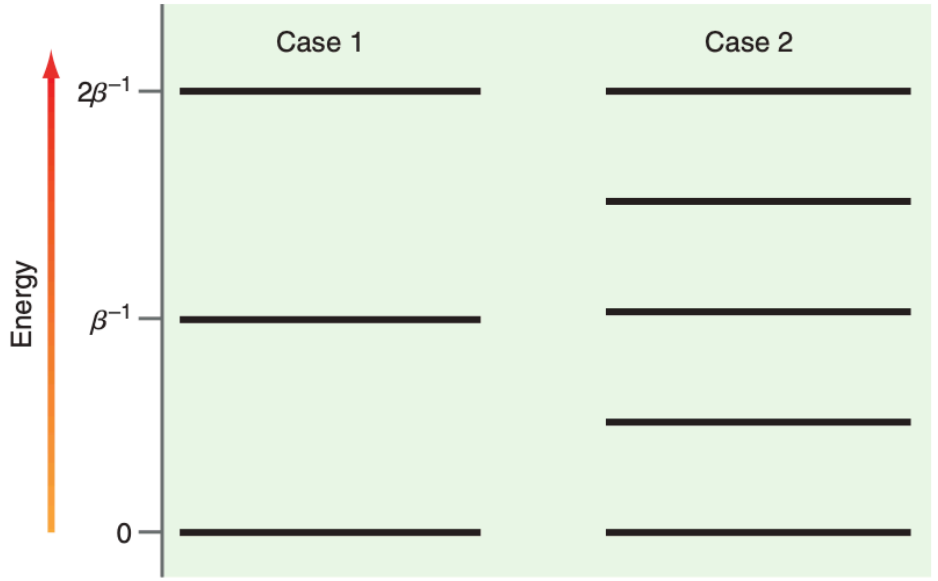
If the energy levels are brought closer together, $q$ increases.

In Case 2 at right, we get

$$p_0 = \frac{e^{-\beta\varepsilon_0}}{q} = \frac{e^{-0}}{2.54} = 0.394$$

$$p_1 = \frac{e^{-\beta\varepsilon_1}}{q} = \frac{e^{-1/2}}{2.54} = 0.239$$

$$p_2 = \frac{e^{-\beta\varepsilon_2}}{q} = \frac{e^{-1}}{2.54} = 0.145$$



# Why care about the partition function?

The partition function encodes all bulk thermodynamic properties in terms of the properties of individual molecules. For example, for the total energy:

$$E = \sum_i \varepsilon_i n_i = N \sum_i \varepsilon_i \frac{e^{-\beta\varepsilon_i}}{q} = -\frac{N}{q}\frac{dq}{d\beta} = -N\frac{d\ln q}{d\beta} = NkT^2\frac{d\ln q}{dT}$$

$$\frac{dq}{d\beta} = -\sum_i \varepsilon_i e^{-\beta\varepsilon_i}$$

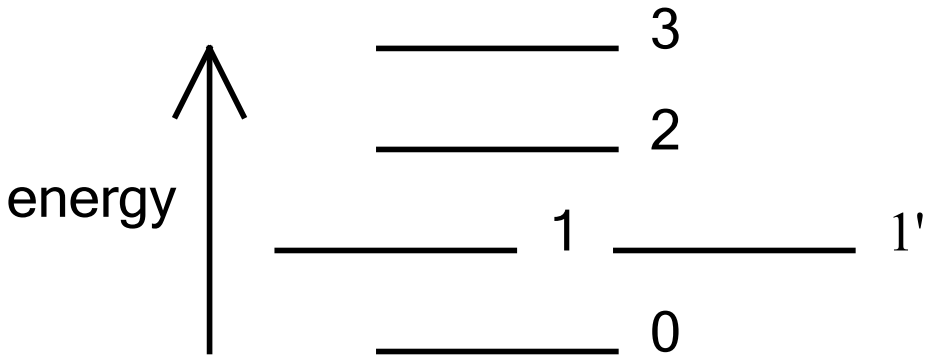
Usually, important thermodynamic functions tend to be derivatives of $q$.

# Degeneracy of molecular states

So far we have referred to *states,* but it is often more natural to talk about energy *levels*. Spectroscopy, for example, resolves differences in energy levels. The difference arises because multiple states can have the same energy, i.e., share the same energy level.

The number $g(\varepsilon)$ of states with energy $\varepsilon$ is called the *degeneracy* of that level.

Shown at right is a molecule with a doubly-degenerate first excited state



# Degeneracy of molecular states

The partition function $q(T)$ can be written equivalently depending on whether you sum over the individual states $i$ or molecular energy levels $\varepsilon_i$

$$q = \sum_i e^{-\beta\varepsilon_i}$$ Summing over states

$$q = \sum_{\varepsilon_i} g(\varepsilon_i) e^{-\beta\varepsilon_i}$$ Summing over levels

Similarly, the Boltzmann distribution for energy levels reads:

$$\frac{n(\varepsilon_j)}{n(\varepsilon_i)} = \frac{g(\varepsilon_j)}{g(\varepsilon_i)} e^{-\beta(\varepsilon_j - \varepsilon_i)}$$

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# Characteristic temperature

The *characteristic temperature* of a system with typical energy spacing $\Delta E$ is

$$\Theta = \Delta E/k \quad \Rightarrow \quad \frac{n_j}{n_i} \sim e^{-\Delta E/kT} = e^{-\Theta/T}$$

Θ is, roughly, the lowest temperature at which excited states start becoming significantly populated.

If $T \gg \Theta$, many states are occupied. The system is "hot".

If $T \ll \Theta$, only the ground state is significantly occupied. The system is "cold".

# Example

Consider a system with characteristic temperature 300 K.

At 300 K, the ratio of molecules in the first excited state to those in the ground state is $e^{-1} = 0.37$

At 3000 K, it is $e^{-0.1} = 0.90$. The first excited state, and many others, are significantly occupied

At 30 K, it is $e^{-10} = 4.5 \cdot 10^{-5}$. Only the ground state is appreciably occupied.

# Summary

Key points:

- Temperature is a property of the most probable configuration
- Zeroth law of thermodynamics
- Kelvin temperature scale; absolute zero
- Molecular partition function is, roughly, the number of thermally accessible states
- Degeneracy should be taken into account
- Characteristic temperature lets us tell whether something is at a high or a low temperature

# Next time

Next time, we will start discussing thermodynamics, starting with the first law. By the end of the week, we will have derived all of classical thermodynamics from scratch.

**Reading:**

E&R *Phys. Chem.* 32.1, 2.1–2.4 **or** E&R *Thermo.* 15.1, 2.1–2.3

**Reminder:**

Remember to complete the in-semester test this week