

Thermal astrophysics – the Origin of Boltzmann factors

Temperature

At its most basic, temperature is the property that objects have in common if they can be in thermal contact without exchanging heat energy. For example, your hand and a radiator are at the same temperature if no heat flows when you put your hand in contact with the radiator. Generally we can talk about the temperature of *systems* rather than just objects. A system is a certain portion of the Universe within some closed surface (the *boundary* of the system) that may be enclosing a solid, liquid, gas or even a batch of photons in space. The system may even be a single atom – the important thing is that we can assign it a temperature.

Consider two systems (1 and 2) which can exchange heat. System 1 contains energy E_1 and system 2 contains E_2 . The total energy of the two systems must be constant, i.e.,

$$E = E_1 + E_2 = \text{constant}. \quad (1)$$

It is the nature of systems that there is usually more than one way in which they can hold their energy. If the system is a molecule for example, it can hold it purely as kinetic energy with a velocity along either the x , y or z axes. It can also hold it purely in internal molecular vibrations, by bending and/or stretching its bonds, or it can be held as various mixtures of these. More complex systems can hold a given amount of energy in an *enormous* number of different ways, each way corresponding to a different quantum state of the system having the same energy. The *degeneracy* of the system, g , is the number of quantum states corresponding to a given energy, and is usually a very big number. For example, the degeneracy of 1 mole of hydrogen atoms is something like $g = 10^{10^{23}}$. For our two systems, their joint degeneracy is simply

$$G = g_1(E_1)g_2(E_2), \quad (2)$$

which we can write as

$$G = g_1(E_1)g_2(E - E_1), \quad (3)$$

because the total energy E is a constant. G is the degeneracy of this macroscopic state of energy E , and depends on how the energy is shared out between 1 and 2.

It turns out that *the combined system is equally likely to be in any one of its accessible quantum states at any particular time*. This is crucially important to the definition of temperature (it's called the 'principle of equal equilibrium probabilities'). It follows that when we put our systems in contact, equilibrium will correspond to the most probable energy division between 1 and 2 – the one that corresponds to more joint states (biggest G) than any other.*

*You may be worried that other divisions of energy, though less probable, could also occur. Worry not. For most practical systems the joint degeneracy peaks unbelievably strongly at the most probable division of energy. Compared with this, other ways of sharing the energy between 1 and 2 are as close to impossible as you can imagine.

Thermal equilibrium will therefore correspond to maximising G with respect to E_1 and E_2 . We will use E_1 as the independent variable and, for convenience, take logs and differentiate with respect to E_1 to maximise $\ln G$. From Equation 3 we get

$$\frac{\partial(\ln G)}{\partial E_1} = \frac{\partial(\ln g_1)}{\partial E_1} + \frac{\partial(\ln g_2)}{\partial E_1} \quad (4)$$

$$= 0 \quad \text{for a maximum.} \quad (5)$$

But $dE_1 = -dE_2$, so equilibrium requires that

$$\frac{\partial(\ln g_1)}{\partial E_1} = \frac{\partial(\ln g_2)}{\partial E_2}, \quad (6)$$

i.e., the two systems have a common value of $\partial(\ln g)/\partial E$ at thermal equilibrium. This fits perfectly with what we think of as temperature. However, we cannot expect our familiar units to correspond with this definition, so we can expect a conversion constant, k , called Boltzmann's constant.

Furthermore, it turns out that the above quantity *increases* as the temperature drops, and that the connection with our familiar concept of thermodynamic temperature, T , is

$$\boxed{\frac{\partial(\ln g)}{\partial E} = \frac{1}{kT}} . \quad (7)$$

The proof that this is indeed the correct relationship with T comes when we compare the predictions of the relation with our experience of, say, classical gases.

Boltzmann factors

We have seen that the temperature of a system (be it 1, 2 or the joint system) is defined in terms of the rate of change of log-degeneracy with energy.* In fact, for small changes near equilibrium (T nearly constant), we can integrate Equation 7 to give

$$g = g_0 \exp(+E/kT), \quad (8)$$

showing that the number of accessible states, g , increases exponentially from its original value, g_0 , when the energy is increased by E above its equilibrium value.

We can use this to compute the probabilities of each of the individual quantum states of a system at temperature T . With this knowledge we can, for example, work out the probability that an atom at a temperature T is in the state corresponding to a particular velocity along the x -axis.

*Although we won't use it here, $k \ln g$ is more usually called the entropy of the system.

Let system 1 be very large indeed, and at temperature T . This system is now so large that its temperature does not change appreciably when small amounts of energy flow in and out – it’s a *reservoir* of heat. Let our smaller system (system 2) be in thermal contact with 1 and in its i th quantum state, with energy ϵ_i (there will be other quantum states with this energy, but we are concentrating on just one of them – a *microstate*). We want the probability of this arrangement, p_i . Again the total energy $E_1 + \epsilon_i$ is a constant, E . From our previous argument it’s clear that p_i is proportional to the overall degeneracy, G , when 2 is in this microstate.

Because we are restricting system 2 to microstate i alone, it does not contribute to the overall degeneracy (there is only one state $i!$), so G is simply equal to $g_1(E_1)$. Hence

$$p_i \propto G \tag{9}$$

$$\propto g_1(E_1) \tag{10}$$

$$\propto \exp(E_1/kT) \quad (\text{from Eqn. 8}) \tag{11}$$

$$\propto \exp(-\epsilon_i/kT) \quad (\text{as } E_1 = E - \epsilon_i). \tag{12}$$

Therefore the probability of finding the smaller system in microstate i is

$$p_i = p_0 \exp(-\epsilon_i/kT) . \quad (13)$$

$\exp(-\epsilon_i/kT)$ is known as the *Boltzmann factor* for a microstate of energy ϵ_i . The normalising constant, p_0 , can be found by using the fact that the system has to be in one of the microstates, so $\sum_i p_i = 1$.

As an example of how this can be applied, consider the thermal speeds of gas atoms along a line-of-sight. This is of great importance in astrophysics, as the distribution determines the shape of a thermally broadened spectral line. If an atom of mass m is in thermal equilibrium at temperature T , the energy of the microstate in which its velocity along the x -axis is v is $\epsilon = mv^2/2$, (the kinetic energy). The probability of seeing such an atom is therefore proportional to $\exp[-mv^2/(2kT)]$, which is a Gaussian distribution. The line profile is therefore also Gaussian (see notes).