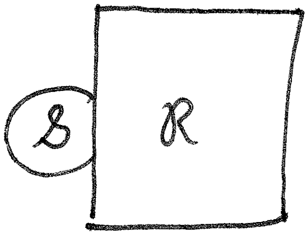
3. Boltzmann Distribution and Free Energy

We continue to explore the concept of *temperature*. This concept applies to a closed system, as we've seen, but it is especially useful for an open system — one in thermal contact with its environment.



To model this, we consider the system $\mathcal{S}$ to be in thermal contact with a much larger system $\mathcal{R}$, called a "reservoir." We imagine that the system and reservoir combined comprise a closed system, with a fixed amount of energy to share. Since the reservoir is very large, the system and reservoir together will seek the most probable configuration. However, we will *not* assume that $\mathcal{S}$ is necessarily very large.

Now consider two particular microscopic states of $\mathcal{S}$, with energy ϵ_1, ϵ_2. (I emphasize these states are completely specified, i.e. they are not degenerate.) What can we say about the probability that the system occupies state 1 or state 2? These probabilities are determined, according to our fundamental assumption, by the number of states accessible to the reservoir, if the system "borrows" energy ϵ_1 or ϵ_2

Thus $$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{g_R(U_0-\varepsilon_1)}{g_R(U_0-\varepsilon_2)}$$

$$= \exp\left[\sigma_R(U_0-\varepsilon_1) - \sigma_R(U_0-\varepsilon_2)\right]$$

- the relative probabilities of the two quantum states of the system are determined by how the entropy of the reservoir changes when the system borrows some energy.

Expand the quantity in brackets in a power series

$$\left(\sigma_R(U_0) - \varepsilon_1 \left.\frac{d\sigma_R}{dU}\right|_{U=U_0} + \frac{1}{2}\varepsilon_1^2 \left.\frac{d^2\sigma_R}{dU^2}\right|_{U=U_0} + \cdots\right)$$

$$-\left(\sigma_R(U_0) - \varepsilon_2 \left.\frac{d\sigma_R}{dU}\right|_{U=U_0} + \frac{1}{2}\varepsilon_2^2 \left.\frac{d^2\sigma_R}{dU^2}\right|_{U=U_0} + \cdots\right)$$

Now recall that entropy is an additive quantity — we expect it to scale linearly with the No. of degrees of freedom of R — e.g. with its volume. Energy also has this property (we say that σ and U are extensive quantities)

We expect $\frac{d\sigma}{dU} = \frac{1}{\tau}$ to be intensive - independent of volume, and $\frac{d^2\sigma}{dU^2} \sim \frac{1}{\text{volume}}$ -- So for a large reservoir, we may ignore the h.o. terms:

We conclude that

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \exp\left(-\frac{\varepsilon_1 - \varepsilon_2}{\tau}\right)$$ where τ is the temperature

of the reservoir, or

$$\boxed{P(\varepsilon) \propto e^{-\varepsilon/\tau}}$$

(energy very large compared to τ is unlikely)

cf 3rd law: as $\tau \to 0$ $\varepsilon \to \varepsilon_{\text{ground}}$

This expression for the probability that the system (in contact with a reservoir at temperature τ) occupies an energy eigenstate with probability ε is called the Boltzmann factor. This is one of the most important equations in statistical physics

To obtain a normalized probability distribution we divide by the Boltzmann factor summed over all states. This quantity, a function of the temperature is called the partition function

$$Z(\tau) \equiv \sum_s e^{-\varepsilon_s/\tau}$$

$$\boxed{P(\varepsilon_s) = \frac{e^{-\varepsilon_s/\tau}}{Z}}$$

We use this probability distribution to compute ensemble averages for open systems -- i.e. for a system in thermal contact with a reservoir.

(We are still using the fundamental assumption — that all accessible states are equally likely — but we are applying it to system and reservoir combined rather than to system alone. And we derive from this assumption the prob. distribution for the system alone.

Then we find, for the ensemble average of the energy:

$$U = \langle \varepsilon \rangle = \sum_s \varepsilon_s P(\varepsilon_s) = \sum_s \frac{\varepsilon_s e^{-\varepsilon_s/\tau}}{Z}$$

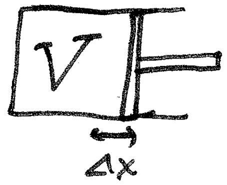
And noticing that $\frac{d}{d\tau} Z(\tau) = \sum_s \varepsilon_s/\tau^2 \, e^{-\varepsilon_s/\tau}$

we have $U = \tau^2 \frac{1}{Z} \frac{d}{d\tau} Z = \tau^2 \frac{d}{d\tau}(\log Z)$

(Note that, even for a closed system, if we identify a part of the system and consider the prob distribution for those degrees of freedom alone, it will be the Boltzmann distribution — we can regard the rest of the system as the reservoir.)

Pressure:

Pressure of e.g. a gas is defined as the force per unit area exerted by the gas on the walls of its container



To compress the gas, we must do work

$$W = F\Delta x = PA\Delta x = -P\Delta V$$

For a *closed* system, the work goes into the internal energy of the system, so

$$\Delta U = -P\Delta V$$

Pressure, then, is a measure of how the energy of the system changes when we change the volume

$$P = -\frac{\partial U}{\partial V}$$

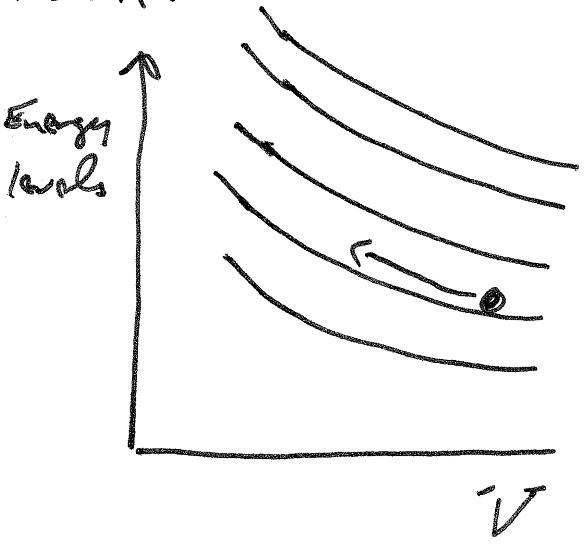
(if the system expands, it *does* work on the piston and loses energy)

One subtlety -- if we want to use statistical physics to study pressure, we must ensure that our fundamental assumption remains valid — that we can continue to regard all accessible states of the system as equally likely during and just after the change in volume. To ensure this, the change must be sufficiently *slow*, slow enough for the system to remain in its equilibrium configuration at all stages during the process.

A slow change, in which the system remains in equilibrium during the change, is called *reversible*. Two kinds of reversible change are especially important:

adiabatic (or *isentropic*), in which the system is thermally isolated during the change or *isothermal*, in which the system remains in contact with a reservoir and is maintained at constant temperature.

To define pressure, we must consider an isentropic change, so that the work done is extracted from the system, and not the reservoir.



From a microscopic point of view, the system has many (closely spaced) energy levels. The energies of the levels change as we change the volume, but quantum states are neither created nor destroyed. Furthermore, if we change the volume very slowly, the system will not be excited from one level to another. Thus an ensemble of states, all with equal probability of being occupied evolves to another such ensemble, with the total number of states *conserved*. Hence the name *isentropic*: a slow change in a closed system preserves the entropy

Pressure may be defined as

$$P = -\left(\frac{\partial U}{\partial V}\right)_\sigma$$ — the derivative is evaluated with the entropy held fixed

From our microscopic discussion, we see that this quantity may also be interpreted as the ensemble average of the derivative of the energy of each state wrt volume

$$P = -\left\langle \frac{d\varepsilon_s}{dV} \right\rangle$$

Thermodynamic Identity

Now consider entropy as a function of U and V. We have learned that

$$\left(\frac{\partial \sigma}{\partial U}\right)_V = \frac{1}{\tau} \qquad -\left(\frac{\partial U}{\partial V}\right)_\sigma = P$$

$\Rightarrow dU = \tau d\sigma - P dV$

From these we can infer $\left(\frac{\partial \sigma}{\partial V}\right)_U$, as follows $\Downarrow$

$$d\sigma(U,V) = \left(\frac{\partial \sigma}{\partial U}\right)_V dU + \left(\frac{\partial \sigma}{\partial V}\right)_U dV$$

$\tau d\sigma = dU + P dV$

Now — suppose U and V change so as to leave σ invariant: $d\sigma = 0$

$$\Rightarrow \left(\frac{\partial \sigma}{\partial U}\right)_V dU = -\left(\frac{\partial \sigma}{\partial V}\right)_U dV \qquad (\text{constant } \sigma)$$

or.. just say $dU = 0 = \tau d\sigma - P dV \Rightarrow \left(\frac{\partial \sigma}{\partial V}\right)_U = P/\tau$

Dividing

$$P \equiv -\left(\frac{\partial U}{\partial V}\right)_\sigma = \left(\frac{\partial \sigma}{\partial U}\right)_V^{-1}\left(\frac{\partial \sigma}{\partial V}\right)_U = \tau\left(\frac{\partial \sigma}{\partial V}\right)_U$$

$$\Rightarrow \left(\frac{\partial \sigma}{\partial V}\right)_U = P/\tau$$

So the differential of entropy has the form

$$d\sigma = \frac{1}{\tau}\,dU + \frac{P}{\tau}\,dV$$

or $\boxed{\tau\, d\sigma = dU + P\,dV}$ "Thermodynamic Identity"

And if we wish, we may regard U as a function of σ and V, satisfying

$$dU = \tau\, d\sigma - P\,dV = T\,dS - P\,dV$$

(written on page 3.7)

(which we could have written down immediately)

$-P\,dV$ can be interpreted as "work done" and $\tau\, d\sigma = T\,dS$ is the "heat added" to the system, which can also change its energy. For reversible changes in an isolated system (no heat exchange with reservoir), we have $dS = 0$.

The Helmholtz Free Energy

Under our fundamental assumption, a system seeks its <u>most probable configuration</u> - it tries to maximize the number of accessible states. Let's consider what this means for a system S in contact with a reservoir R — a system maintained at temperature τ.

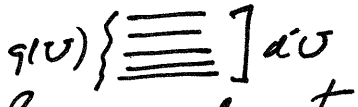
Now there are two conflicting demands on the system. On the one hand, the system, because of the Boltzman factor

$$P(\varepsilon) \propto e^{-\varepsilon/\tau}$$

wants to minimize its own ~~entropy~~ energy (because this is what <u>maximizes</u> the entropy of the reservoir) on the other hand, the system wants to maximize its <u>own</u> entropy.

The probability distribution for S has a maximum at some value of the system energy U_S — this is its most probable configuration. Furthermore, if the system is large (but still small compared to R) the distribution is sharply peaked, so U_S has a (nearly) definite value in equilibrium.

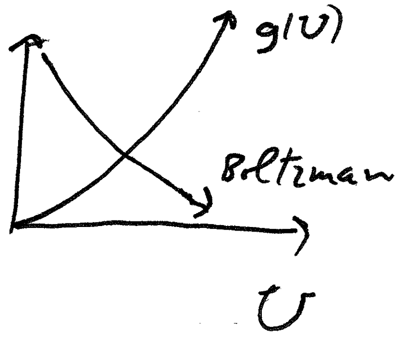
We may represent the



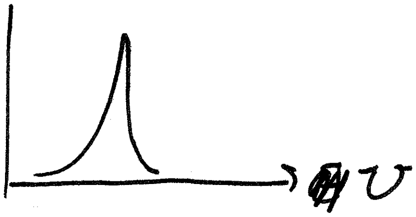
(close) distribution of energy levels as a <u>density</u> of levels per unit energy

Then $\sum_s e^{-\varepsilon_s/\tau} \sim \int dU\, g(U)\, e^{-U/\tau}$

$$= \int dU \exp\left[\sigma - U/\tau\right]$$



We see here the competition between the system's desire to minimize its energy and maximize its entropy



A peak arises at the most probable value of U

This peak arises where the argument of the exponential is stationary, or

$$0 = \frac{d}{dU}\left[U - \tau\sigma\right]$$

(recall that τ is a constant – fixed by the reservoir)

The quantity $F = U - \tau\sigma$ is called the Helmholtz free energy -- it is the quantity that a system at a fixed temperature tries to minimize as it seeks its most probable configuration

Above I described F as a function of U with a parameter τ. But it is usually more convenient to think of it in a different way:

we suppose that U has been chosen to attain the value that minimizes this expression. *Then* we obtain a function of τ

$$F(\tau) = U - \tau\sigma \Big|_{\text{stat } U}$$

i.e. evaluate where stationary wrt U, that is, U is chosen so

$$1 = \tau \frac{d\sigma}{dU}$$

or $\dfrac{\partial U}{\partial \sigma} = \tau$] we have just re*expressed* that the system in contact with the reservoir finds its most probable configuration by coming to temperature equilibrium with the reservoir.

(This way of obtaining a function of τ from a function of U is called a "Legendre transform.")

To see why $F(\tau)$ is a useful quantity, we consider what happens if we *vary* the temperature, and vary the volume. If we make reversible changes in V and τ, U adjusts so that the system remains in its most probable configuration all the while

At fixed volume, this means

$$dF = dU - \tau d\sigma - \sigma d\tau$$

But with $dU = \tau d\sigma \Rightarrow dF = -\sigma d\tau$

or $\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma$

On the other hand, suppose we vary the volume with the temperature fixed. Then we may use the thermodynamic relation

$$dU = \tau d\sigma - p\,dV$$

and find $dF = -p\,dV$ or $\left(\frac{\partial F}{\partial V}\right)_\tau = -p$

so the differential of F is

$$\boxed{dF = -\sigma d\tau - p\,dV} \rightsquigarrow$$

change in free energy reflects work done at fixed τ

We have found an alternative expression for the pressure $\longrightarrow$ $p = -\frac{\partial F}{\partial V}\Big|_\tau$

$$p = -\frac{\partial}{\partial V}\left(U - \tau\sigma\right)\Big|_\tau$$

$$= -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau\left(\frac{\partial \sigma}{\partial V}\right)_\tau$$

or the work done is $p\,dV = -dU + \tau d\sigma$