

F.4 Entropy



What energy conversions are happening/going to happen?

Dude's gravitational potential energy to kinetic energy

Dude's kinetic energy to water's internal energy



What energy conversions are happening/going to happen?

Water's internal energy to dude's kinetic energy.

Dude's kinetic energy to gravitational potential energy.

F.4 Entropy

First law doesn't not in principle preclude the last scenario from happening, as energy is conserved either way. Consider 'orderliness' of the energy.



Energy goes from gravitational potential energy which is 'ordered', to internal energy, which is more 'disordered', random and chaotic.

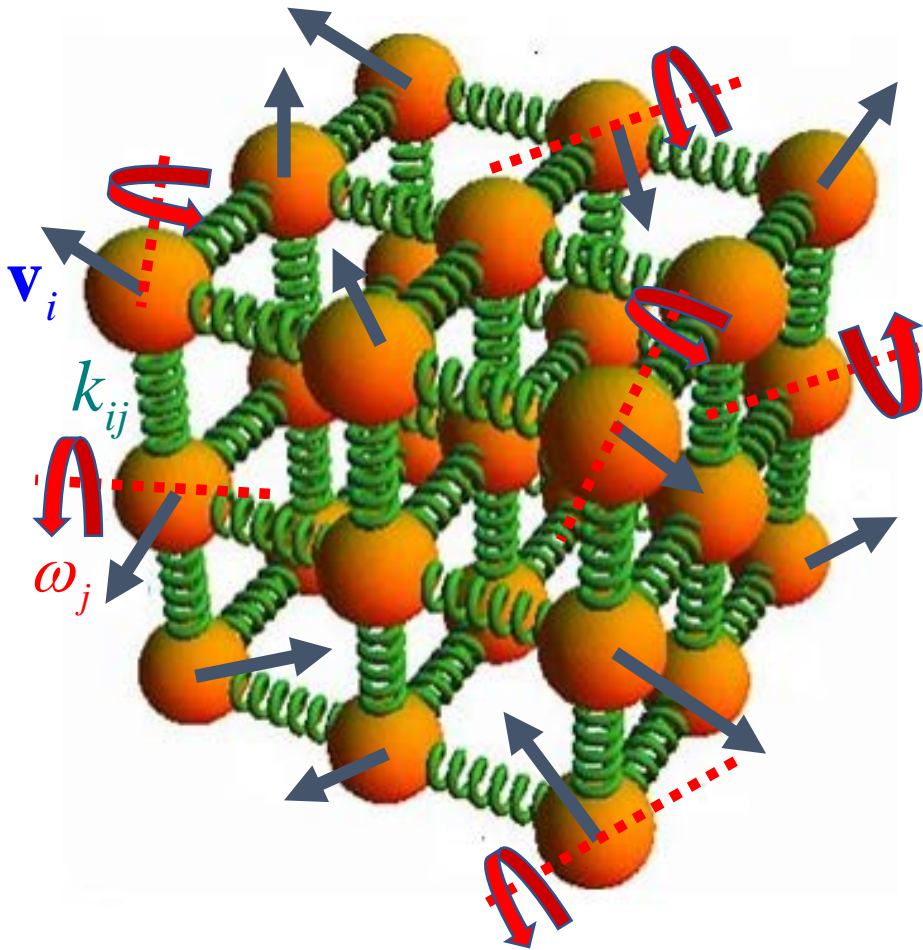


Energy goes from 'disordered' internal energy, to 'ordered' gravitational potential energy,

Apparently, energy conversions that get more disordered are allowed, but ones which get more ordered are not.

F.4 Entropy

So we need a quantitative measure of ‘disorder’, if we are to figure out if an energy conversion is allowed or not. And this measure is called: entropy.



Consider again some object at temperature T . The instantaneous ‘state’ of the object is the specification of each of its constituent particles’ *position* and *velocity*.

As a consequence of its temperature, its constituent particles are rapidly changing both their positions, and velocities. And so the object is rapidly changing its state.

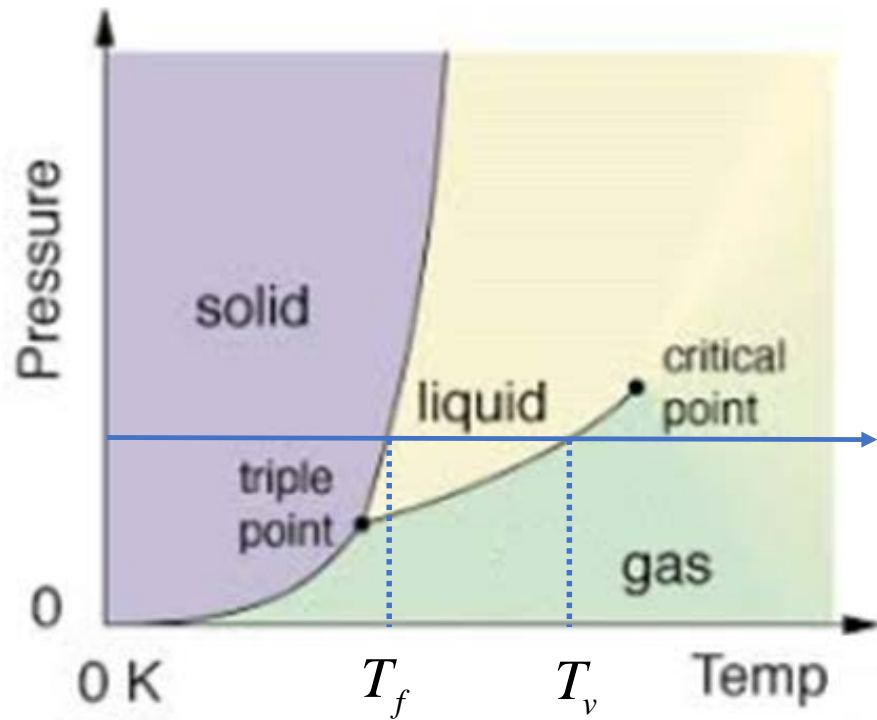
$$\Omega = \# \text{ of states the system fluctuates through in some small time } \tau$$

The entropy, S , of the system is defined in terms of Ω . Formally,

$$S = k_B \ln \Omega$$

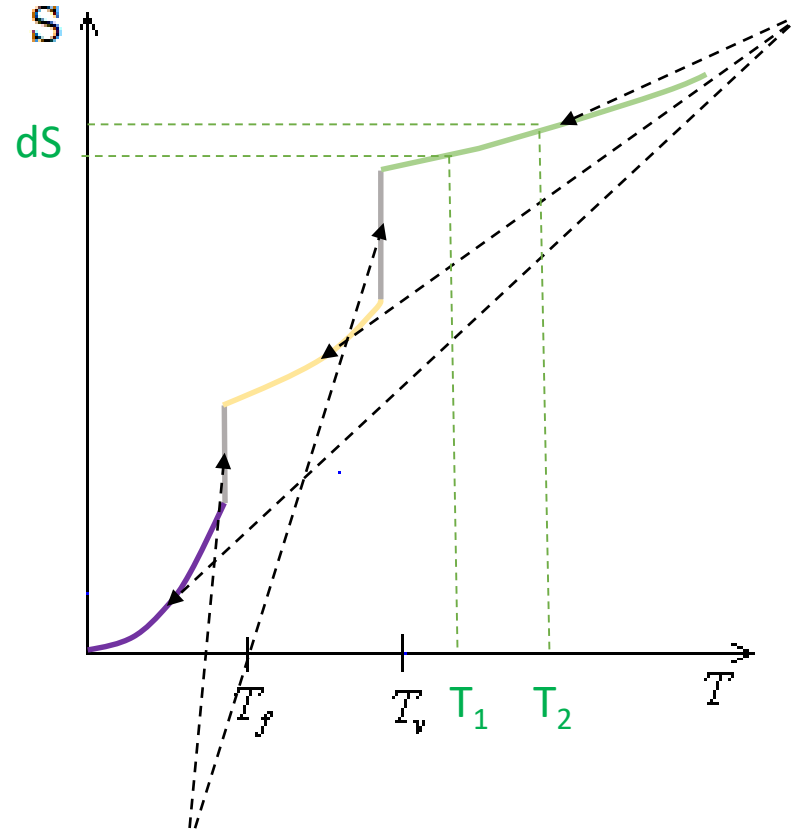
F.4 Entropy

But it would just about be impossible to calculate S from this formula, as it involves keeping track of all the object's $\sim 10^{23}$ particles. Fortunately, just like E_{internal} , S depends on just three parameters: T , V , N , i.e. $S(T,V,N)$. If we focus solely on the T -dependence, we'd get something like this:



Temperature of fusion,
where solid becomes liquid.

Temperature of vaporization,
where liquid becomes gas.



$$dS = \frac{dE}{T}$$

integrating, we get:

$$\Delta S = \int_{T_1}^{T_2} \frac{dE}{T}$$

Now $dE = mcdT$, so,

$$\Delta S = \int_{T_1}^{T_2} \frac{mcdT}{T}$$

$$\Delta S = \int \frac{dE}{T} = \frac{1}{T} \int dE = \frac{1}{T} mL \longrightarrow \Delta S = \frac{mL}{T}$$

F.4 Entropy

Say we put 2kg of steam at 130°C in the freezer. If we cooled it half-way to ice, what would be its change in entropy?

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_v} \frac{mcdT}{T} - \frac{mL_v}{T_v} + \int_{T_v}^{T_f} \frac{mcdT}{T} - \frac{(m/2)L_f}{T_f} \\&= \int_{273+130}^{273+100} \frac{(2\text{ kg})\left(1.98 \frac{\text{kJ}}{\text{kg K}}\right)dT}{T} - \frac{(2\text{ kg})\left(2256 \frac{\text{kJ}}{\text{kg}}\right)}{T_v} + \int_{273+100}^{273+0} \frac{(2\text{ kg})\left(4.18 \frac{\text{kJ}}{\text{kg K}}\right)dT}{T} - \frac{(1\text{ kg})\left(333 \frac{\text{kJ}}{\text{kg}}\right)}{T_f} \\&= (2\text{ kg})\left(1.98 \frac{\text{kJ}}{\text{kg K}}\right) \ln\left(\frac{273+100}{273+130}\right) - \frac{(2\text{ kg})\left(2256 \frac{\text{kJ}}{\text{kg}}\right)}{373} + (2\text{ kg})\left(4.18 \frac{\text{kJ}}{\text{kg K}}\right) \ln\left(\frac{273}{273+100}\right) - \frac{(1\text{ kg})\left(333 \frac{\text{kJ}}{\text{kg}}\right)}{273} \\&= -0.306 \frac{\text{kJ}}{\text{K}} - 12.1 \frac{\text{kJ}}{\text{K}} - 2.6 \frac{\text{kJ}}{\text{K}} - 1.22 \frac{\text{kJ}}{\text{K}} \\&= -16.2 \frac{\text{kJ}}{\text{K}}\end{aligned}$$

F.4 Entropy

For some purposes, though, we *do* need to know how $S(T,V,N)$ depends on volume. And we can work this out for the three special cases we considered before: ideal gas, Van der Waals gas, ideal solid. Saving you the agony (if you want, you can look at the Summary in Polylearn for a derivation of the results)...it all starts with the formula $S = k_B \ln \Omega$, and ends up with....

$$S = Nk_B \ln \left(\frac{T^{f/2} V}{\Phi N} \right) \quad \text{entropy of ideal gas}$$

Φ = don't ask, but it's just a constant.

$$S = Nk_B \ln \left(\frac{T^{f/2} (V - bN)}{\Phi N} \right) \quad \text{entropy of Van der Waals gas}$$

Φ = I said, don't ask, but it's just another constant.

b = volume of a typical particle in the gas

$$S = Nk_B \ln \left(\frac{T^{f/2} V_{micro}}{\Phi N} \right) + \alpha \beta (V - \nu) \quad \text{entropy of ideal solid}$$

Φ = really?

V_{micro} = volume typical atom oscillates about in equilibrium

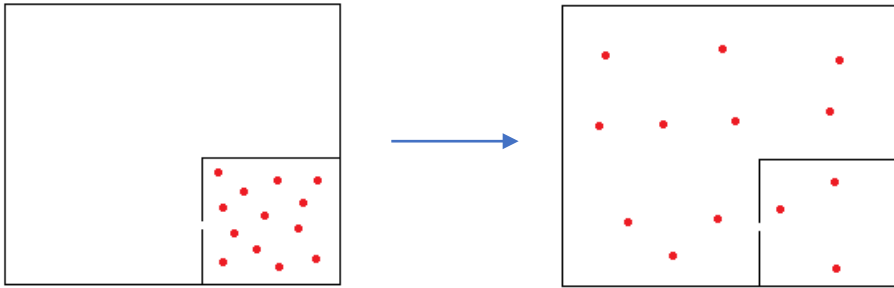
α = coefficient of thermal expansion

β = bulk modulus

ν = approximate volume of solid at $T = p = 0$.

F.4 Entropy

Question 3. Suppose you have 0.77 mol of an ideal gas kept in a container of volume $V = 0.04\text{m}^3$, pressure $p = 5\text{atm}$, temperature $T = 400\text{K}$. Then you open the container and let it expand into a larger insulated container of volume $V = 0.20\text{m}^3$ (volume includes original container).
 (a) What will be the change in energy of the gas? (b) What will be its change in entropy?



We can get change in energy from the 1st law:

$$Q + W = \Delta E_{\text{mech.}} + \Delta E_{\text{int.}}$$

$$0 + 0 = 0 + \Delta E_{\text{int.}}$$

$$\Delta E_{\text{int.}} = 0$$

Note that since $E_{\text{ideal gas}} = (f/2)Nk_B T$, this means that T doesn't change either....

And we can get the change in entropy from our equation.

$$\Delta S = S_2 - S_1$$

$$= Nk_B \ln \left(\frac{T_2^{f/2} V_2}{\Phi N} \right) - Nk_B \ln \left(\frac{T_1^{f/2} V_1}{\Phi N} \right)$$

$$= Nk_B \ln \left(\frac{T_2^{f/2} V_2}{T_1^{f/2} V_1} \right) \quad (\text{magic math, otherwise known as } \ln a - \ln b = \ln(a/b))$$

$$= nR \ln \left(\frac{V_2}{V_1} \right) \quad \text{using identity } Nk_B = nR, \text{ and fact that } T \text{ didn't change}$$

$$= (0.77\text{mol}) \left(8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \ln \left(\frac{0.2}{0.04} \right)$$

$$= 10.3\text{J/K}$$