Review of Einstein Solid

We have determined

- Multiplicity: $\Omega(N,q)$

$$\Omega(N,q) = \left(\frac{qe}{N}\right)^N \qquad \text{where } q >> N >> 1$$

$u = \varepsilon q = q h f$

- Entropy: $S = k \ln\Omega$

$$S = k\ln\left(\frac{qe}{N}\right)^N = Nk\left[\ln\left(\frac{q}{N}\right)+1\right] = Nk\ln U - Nk\ln(\varepsilon N) + Nk$$

no. of oscillators

- Temperature-Energy relation:

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1} = \left(\frac{Nk}{U}\right)^{-1} \qquad U = NkT \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = Nk$$

Determination of Entropy

- Example of heating 200 g water from 20 ºC to 100 ºC

calculate $\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T}\, dT$ relatively constant

C_V of 200 g H_2O is 840 J/K ← over temp range

$$\Delta S = C_V \int_{293}^{373} \frac{1}{T}\, dT$$

$$= [840 \text{ J/K}]\left[\ln\left(\frac{373}{293}\right)\right]$$

$$\cong 200 \text{ J/K} \rightarrow 1.5\times10^{25} k$$

knowing C_V → absolute zero

$$S_f - S(0) = \int_0^{T_f} \frac{C_V}{T}\, dT$$

in principle $S(0) = 0$

$\Omega = 1 \rightarrow S = 0$

Residual Entropy

- Some solids are composed of molecules, frozen in place

So $S(0)$ is effectively non-zero

→ hydrogen OH bonds can have H_2O molecules oriented in different ways

→ no change in overall energy

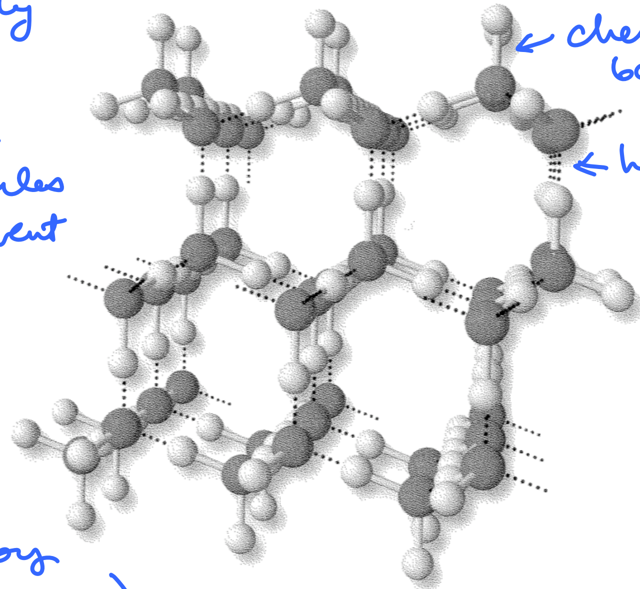
have $\Omega > 1$

→ same energy

residual entropy

$S = k \ln(\Omega \text{ at } 0K)$

water ice



chemical bond

hydrogen bond

Multiplicity of an Ideal Gas

- More complicated than previous examples
  - Ω is now a function of volume as well as energy (U) and total number of particles
- Start with a monatomic ideal gas
  - Kinetic energy of U and in container of volume V
  - Just one atom in the gas!
- What does the multiplicity of this system depend on?
  - Number of different ways of "arranging" gas atom
  - Depends on position and momentum

Ideal Gas

Multiplicity depends on:

- Volume
  - Double the size of the gas container and twice as many "position" states are available to the gas atom
- Momentum
  - The more different momentum vectors the gas atom can have, the more states that are available

$p = mv$

Can think in terms of position space and momentum space…

One Atom Ideal Gas

- Momentum space
  - A point in momentum space is coordinate in (p_x, p_y, p_z)
  - This corresponds to the momentum vector for the gas atom
- For one atom ideal gas, multiplicity is

$$\Omega_1 \propto V\, V_p$$

using volume analogy for position and momentum space

- Can calculate volume available in position space, but what momenta are available for the gas atom?
  - Limited by kinetic energy of gas atom

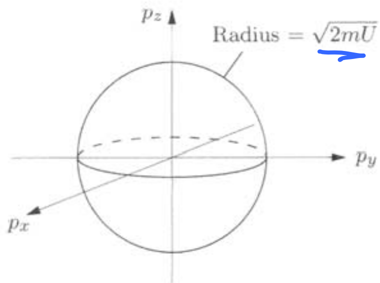
$$U = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

fixed in system

One Atom Ideal Gas (cont.)

$$U = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

$$\boxed{\left(p_x^2 + p_y^2 + p_z^2\right) = 2mU}$$



- Equation defines surface of a sphere in momentum space with radius of $\sim\sqrt{U}$
  - "Volume" of accessible states in the momentum space is really the surface area of this sphere $\sim R^2 \sim U$

Two Atom Ideal Gas

Now, what if there are two particles in the ideal gas

- How will this change the multiplicity?
  - Position space: volume goes from V to V^2
  - Momentum space: not so easy

$$\left(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2\right) = 2mU$$

  - Surface area of a 6-dimensional hypersphere with radius $\sim\sqrt{U}$: function of r^{d-1}

d = dimensions
r = radius

d = 2 area has circumference of circle $2\pi r$

d = 3 $4\pi r^2$ surface area of sphere

relation is $d-1$
radius

N Atom Ideal Gas

Extend this to N atom ideal gas

- Position space: V^N
- Momentum space:

Surface area of 3N-dimensional hypersphere with radius $\sqrt{U}$

$$V_p \propto \left(\sqrt{2mU}\right)^{3N-1} \quad d-1$$

- Looking at limit for large N

$$\Omega_N \propto V^N V_p = f(N) V^N U^{3N/2} \quad \leftarrow \text{for } N \text{ large} \quad \frac{3N}{2}-1 \approx \frac{3N}{2}$$

From Quantum Mechanics,

$$\Omega_N \approx \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{(3N/2)!}\left(\sqrt{2mU}\right)^{3N}$$

Entropy of an Ideal Gas

$$\Omega_N \approx \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{(3N/2)!}\left(\sqrt{2mU}\right)^{3N}$$

$$\ln \Omega_N = \ln\left\{\frac{V^N}{h^{3N}}\pi^{3N/2}(2mU)^{3N/2}\right\} - \ln N! - \ln\left(\frac{3N}{2}\right)!$$

$$\ln N! + \ln\left(\frac{3N}{2}\right)! \cong N\ln N - N + \frac{3N}{2}\ln\left(\frac{3N}{2}\right) - \frac{3N}{2}$$

$$= N\ln\left[N\left(\frac{3N}{2}\right)^{3/2}\right] - \frac{5N}{2}$$

$$S = k\ln\Omega_N = k\ln\left(\frac{V^N}{h^{3N}}\pi^{3N/2}(2mU)^{3N/2}\right)$$

$$- Nk\ln\left[N\left(\frac{3N}{2}\right)^{3/2}\right] + \frac{5Nk}{2}$$

↳ collect terms to get eq. on next page.

Entropy of an Ideal Gas (cont.)

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right]$$

Sackur-Tetrode Equation

- For example, a mole of He at room temperature and atmospheric pressure:
  - Use ideal gas law ($V=RT/P$); $U=3RT/2$; mass of He = 4 m_p

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right] \approx Nk\big(\ln(330{,}000)+2.5\big) = 126\ \mathrm{J/K}$$

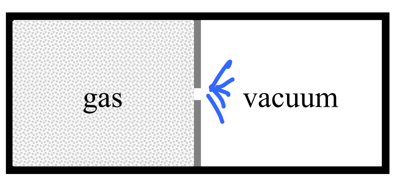
  - Entropy of an ideal gas depends only on its volume, energy and number of particles
  - If we only change the volume, then the entropy change is:

$$\Delta S = Nk\ln\frac{V_f}{V_i} \qquad (U, N \text{ fixed})$$

Creating Entropy

- Free Expansion
  - No heat, no work, but entropy increases!

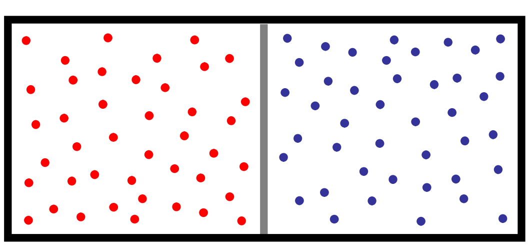
$\Delta U = Q + W = 0$



- Entropy of Mixing

$\Delta S_A = Nk\ln\left(\frac{V_f}{V_i}\right)$
$= Nk\ln 2$

$\Delta S_{total} = \Delta S_A + \Delta S_B$
$= 2Nk\ln 2$



A B

for A & B
same N
same U
same V

More on Multiplicity of Ideal Gas

$$\Omega_N \approx \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{(3N/2)!}\left(\sqrt{2mU}\right)^{3N}$$

$\Omega \propto U^{Nf/2}$

Ideal gas particles are indistinguishable

uncertainty principle

spread in x Δx spread in p_x Δp_x

$\Delta x \Delta p_x \approx h$

$\left[\frac{L}{\Delta x}\right]$ number of distinct states

$\rightarrow \left[\frac{L}{\Delta x}\right]\left[\frac{L_p}{\Delta p_x}\right] = \frac{L L_p}{h}$ in 3D $\frac{V V_p}{h^3}$ for 1 atom

exponent is $\frac{1}{2} \times 3N$ total degrees of freedom in monatomic gas

$\Omega_N = \left(\frac{eq}{N}\right)^N$ for Einstein solid

$f = 2$ per oscillator

$Nf/_2 = N$