Entropy of mixing gas Masatsugu Sei Suzuki Department of Physics, SUNY at Binghamton (Date: Septemnrt 09, 2017)

1. Adiabatic free expansion (irreversible process) (from lecture note on Phys.131, General Physics)



An adiabatic free expansion of an ideal gas i.e. where a greater volume suddenly becomes available to the gas is an irreversible process which proceeds through a chaotic non-equilibrium path. Nonetheless we can characterize the beginning and end points and the net values of relevant changes in energy. Since the gas expands against a vacuum it does no work and thus

 $W_{i \to f} = 0$.

since there is no motion of the boundary (nothing to push against; there is no movable piston). Combining this with our requirement that the process is adiabatic, we have

$$E_{i \to f} = Q_{i \to f} + W_{i \to f} = 0 + 0 = 0$$

If we are dealing with an ideal gas, then the absence of a change in the internal energy implies that the temperature is the same before and after the expansion even though no temperature is defined during the irreversible process: $T_f = T_i$.

In order to calculate the entropy of this process, we need to find an equivalent reversible path that shares the same initial and final state. A simple choice is an isothermal, reversible expansion in which the gas pushes slowly against a piston. Using the equation of state for an ideal gas this implies that

$$P_i V_i = P_f V_f$$

The initial and final states $a(P_i, V_i)$ and $b(P_f, V_f)$ are shown on the *P*-*V* diagram. Even though the initial and final states are well defined, we do not have intermediate equilibrium states that take us from the state $a(P_i, V_i)$ and the state $b(P_f, V_f)$.



Fig. Note that the irreversible process (green line) cannot be described in such a line in the P-V phase diagram. The isothermal process is denoted by the blue line.

We thus replace the free expansion with an isothermal expansion that connects states i and f. Then the entropy can be calculated as follows (the isothermal process)

$$\Delta E = 0$$

$$dQ_r = -dW = PdV = \frac{RT}{V}dV$$
 (reversible process)

$$\Delta S = \int_{V_i}^{V_f} \frac{dQ_r}{T} = R \int_{V_i}^{V_f} \frac{dV}{V} = R \ln(\frac{V_f}{V_i})$$

Since $V_f > V_i$, ΔS is positive. This indicates that both the entropy and the disorder of the gas increase as a result of the irreversible adiabatic expansion.

((Note))

$$dQ_r = TdS$$
 (reversible process)

$$\frac{dQ_{irr}}{T} \le dS$$

Even if $dQ_{irr} = 0$ (adiabatic process),

$$dS \ge 0$$
.

Note that dS > 0 for the irreversible process and dS = 0 for the reversible process.

2. The entropy for the adiabatic free expansion (microscopic states)

Entropy can be treated from a microscopic viewpoint through statistical analysis of molecular motions. We consider a microscopic model to examine the free expansion of an ideal gas. The gas molecules are represented as particles moving randomly. Suppose that the gas is initially confined to the volume V_i . When the membrane is removed, the molecules eventually are distributed throughout the greater volume V_f of the entire container. For a given uniform distribution of gas in the volume, there are a large number of equivalent microstates, and the entropy of the gas can be related to the number of microstates corresponding to a given macro-state.



Fig. The volume of the system in the initial state is V_i (the macrostate). The volume of cell (the microstate) is V_m . The number of cells (sites) is given by the ratio V_i/V_m .

We count the number of microstates by considering the variety of molecular locations available to the molecules. We assume that each molecule occupies some microscopic volume V_m . The total number of possible locations of a single molecule in a macroscopic initial volume V_i is the ratio

$$w_i = \frac{V_i}{V_m},$$

which is a very large number. The number w_i represents the number of the microstates, or the number of available sites. We assume that the probability of a molecule occupying any of these sites are equal.

Neglecting the very small probability of having two molecules occupy the same site, each molecule may go into any of the w_i sites, and so the number of ways of locating N molecules in the volume becomes

$$W_i = w_i^N = \left(\frac{V_i}{V_m}\right)^N.$$

Similarly, when the volume is increased to $V_{\rm f}$, the number of ways of locating N molecules increases to

$$W_f = w_f^N = \left(\frac{V_f}{V_m}\right)^N.$$

Then the change of entropy is obtained as

$$\Delta S = S_f - S_i$$

= $k_B \ln W_f - k_B \ln W_i$
= $k_B \ln \left(\frac{V_f}{V_m}\right)^N - k_B \ln \left(\frac{V_i}{V_m}\right)^N$
= $Nk_B [\ln(V_f) - \ln(V_m)] - Nk_B [\ln(V_i) - \ln(V_m)]$
= $Nk_B [\ln(V_f) - \ln(V_i)]$
= $Nk_B \ln(\frac{V_f}{V_i})$

When $N = N_A$, we have

$$\Delta S = N_A k_B \ln(\frac{V_f}{V_i}) = R \ln(\frac{V_f}{V_i})$$

We note that the entropy S is related to the number of microstates for a given macrostate as

$$S = k_B \ln W$$

The more microstates there are that correspond to a given macrostate, the greater the entropy of that macrostate. There are many more microstates associated with disordered macrostates than with ordered macrostates. Therefore, it is concluded that the entropy is a measure of disorder. Although our discussion used the specific example of the adiabatic free expansion of an ideal gas, a more rigorous development of the statistical interpretation of entropy would lead us to the same conclusion.

3. Entropy change of mixing gas

((Kubo, Thermodynamics))

Two kinds of ideal gases at equal pressure and temperature, initially separated into two containers, are mixed by diffusion. Show that the entropy is increased in this process by an amount

$$\Delta S = -R[n_1 \ln(\frac{n_1}{n_1 + n_2}) + n_2 \ln(\frac{n_2}{n_1 + n_2})]$$

where n_1 and n_2 are the moles of components gasses. Assume that no change in pressure and temperature occurs due to the diffusion and the partial pressure of each gas in the mixture is proportional to the molar concentration.



Fig. Initial state. Two gases are separated into two containers by a wall.

$$T, P, V_1 + V_2, n_1 + n_2$$

Fig. Final state. The wall is removed adiabatically.

Since

$$\Delta U = \Delta Q = 0$$

the temperature does not change (adiabatic free expansion).

((Solution))

For the ideal gas, the entropy S is derived as follows,

$$dU = TdS - PdV = nC_V dT$$

PV = nRT

$$dS = \frac{P}{T}dV + n\frac{C_V}{T}dT = nR\frac{dV}{V} + n\frac{C_V}{T}dT$$

Then we have the entropy S as

$$S = nR\ln V + nC_V \ln T$$
$$= nR(\ln V + \frac{3}{2}\ln T)$$

$$S = nR \ln V + nC_V \ln(\frac{PV}{nR})$$

= $nR \ln V + nC_V [\ln P + \ln V - \ln(nR)]$
= $n(R + C_V) \ln V + nC_V \ln P - nC_V \ln(nR)$
= $n[C_P \ln V + C_V \ln P] - nC_V \ln(nR)$

where we use $C_V = \frac{3}{2}R$.

Here we consider the adiabatic free expansion of two gases independently.



is the superposition of two states such that



(a) Adiabatic free expansion of gas-1 into the vacuum space



$$PV_1 = n_1 RT, \qquad V_1 = \frac{n_1 RT}{P}$$

After the adiabatic free expansion for the gas 1 into vacuum space (the right side), we have such a state



Note that

$$P_1(V_1 + V_2) = n_1 RT$$
, $P_1 = \frac{n_1}{V_1 + V_2} RT$

(b) Adiabatic free expansion of the gas-2 into the vacuum space



$$PV_2 = n_2 RT, \qquad V_2 = \frac{n_2 RT}{P}$$

After the adiabatic free expansion of the gas-2 into the vacuum space (the left side)



$$P_2(V_1 + V_2) = n_2 RT$$
, $P_2 = \frac{n_2}{V_1 + V_2} RT$

The final pressure is

$$P_f = P_1 + P_2 = (n_1 + n_2) \frac{RT}{V_1 + V_2}$$

Change of entropy for mixing gas (c) The change of entropy for the gas-1

$$\Delta S_1 = [n_1 R \ln(V_1 + V_2) + n_1 C_V \ln T] - [n_1 R \ln(V_1) + n_1 C_V \ln T]$$
$$= n_1 R \ln(\frac{V_1 + V_2}{V_1})$$

The change of entropy for the gas-2

$$\Delta S_2 = [n_2 R \ln(V_1 + V_2) + n_2 C_V \ln T] - [n_2 R \ln(V_2) + n_2 C_V \ln T]$$
$$= n_2 R \ln(\frac{V_1 + V_2}{V_2})$$

The total change of entropy (universe) is

$$\Delta S = \Delta S_1 + \Delta S_2$$

= $n_1 R \ln(\frac{V_1 + V_2}{V_1}) + n_2 R \ln(\frac{V_1 + V_2}{V_2})$
= $-[n_1 R \ln(\frac{V_1}{V_1 + V_2}) + n_2 R \ln(\frac{V_2}{V_1 + V_2})]$
= $-R[n_1 \ln(\frac{n_1}{n_1 + n_2}) + n_2 \ln(\frac{n_2}{n_1 + n_2})]$

or

$$\Delta S = -R[n_1 \ln(\frac{n_1}{n_1 + n_2}) + n_2 \ln(\frac{n_2}{n_1 + n_2})]$$
(1)

which is a positive quantity So the diffusion is an irreversible process.

We use the following notations.

$$n_1 + n_2 = n$$

 $n_1 = nx$, $n_2 = n(1 - x)$

Then we have

$$\Delta S = -nR[x \ln x + (1-x)\ln(1-x)] = -Nk_B[[x \ln x + (1-x)\ln(1-x)]]$$



Fig. Entropy *S* vs *x*. We make a plot of $\frac{\Delta S}{Nk_B}$ vs *x* for 0 < x < 1.

4. Gibbs paradox

From the above, we see that the increase of entropy due to diffusion depends only on the numbers of moles n_1 and n_2 , but not on their nature, for example, on their molar weight. So far as the increase of entropy is concerned, then, it makes no difference whether the gases are more or less "similar" chemically. This leads us to make a strange inference. If the two gases are assumed to be identical, the increase of entropy is obviously zero, because then no change of state occurs at all. This is called the Gibbs paradox.

As understood by Gibbs, this is a misapplication of Gibbs' non-extensive entropy quantity. If the gas particles are distinguishable, closing the doors will not return the system to its original state - many of the particles will have switched containers. There is a freedom in what is defined as ordered, and it would be a mistake to conclude the entropy had not increased. In particular, Gibbs' non-extensive entropy quantity for an ideal gas was not intended for varying numbers of particles. The paradox is averted by concluding the indistinguishability (at least effective indistinguishability) of the particles in the volume. This results in the extensive Sackur–Tetrode equation for entropy.

5. Sackur–Tetrode equation for entropy.

(a). Canonical ensemble

We consider a calculation of the partition function of Maxwell-Boltzmann system (ideal M-B particles). The system consists of *N* particles (distinguishable).

The enegy of the system is given by

$$E_i = \varepsilon_1 n_1 + \varepsilon_2 n_2 + \dots + n_s \varepsilon_s$$

where $\varepsilon_1, \varepsilon_2, ..., \varepsilon_s$ are the energy levels (quantized, discrete). The total number of particles is

$$N = n_1 + n_2 + n_3 + \dots + n_s,$$

State $|\varepsilon_1\rangle$ with energy ε_1 level n_1 particles
State $|\varepsilon_2\rangle$ with energy ε_2 level n_2 particles
.....
State $|\varepsilon_s\rangle$ with energy ε_s level n_s particles

The way to choose n_1 particles with the state $|\varepsilon_1\rangle$, n_2 particles with the state $|\varepsilon_2\rangle$, ..., and n_s particles with the state $|\varepsilon_s\rangle$ from N particles is evaluated as

$$\frac{N!}{n_1!n_2!...n_s!}$$

where these particles are distinguishable. Then the partition function for the M-B particles (particle number is N) based on the canonical ensemble

$$Z_{C}(\beta) = \sum_{n_{1}} \sum_{n_{2}} \dots \sum_{n_{s}} \frac{N!}{n_{1}!n_{2}!\dots n_{s}!} \exp[-\beta(\varepsilon_{1}n_{1} + \varepsilon_{2}n_{2} + \dots + n_{s}\varepsilon_{s})]\delta_{n_{1}+n_{2}+\dots+n_{s},N}$$
$$= \sum_{n_{1}} \sum_{n_{2}} \dots \sum_{n_{s}} \frac{N!}{n_{1}!n_{2}!\dots n_{s}!} (e^{-\beta\varepsilon_{1}})^{n_{1}} (e^{-\beta\varepsilon_{2}})^{n_{2}} \dots (e^{-\beta\varepsilon_{s}})^{n_{s}} \delta_{n_{1}+n_{2}+\dots+n_{s},N}$$
$$= (e^{-\beta\varepsilon_{1}} + e^{-\beta\varepsilon_{2}} + \dots + e^{-\beta\varepsilon_{s}})^{N}$$
$$= [Z_{C1}(\beta)]^{N}$$

where $\delta_{n_1+n_2+...+n_s,N}$ means the condition of total particle number kept constant. We note that $Z_{C1}(\beta)$ is the partition function for the one particle system.

$$Z_{C1}(\beta) = e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \dots + e^{-\beta\varepsilon_3}$$

Suppose that $|\varepsilon_i\rangle = |\mathbf{k}\rangle$,

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

instead of ε_i .

$$\hat{H}|\mathbf{k}\rangle = \varepsilon_{\mathbf{k}}|\mathbf{k}\rangle$$

(b) Calculation of $Z_{C1}(\beta)$

Now we calculate the partition function (canonical ensemble) using the density of state for the one particle system

$$Z_{C1}(\beta) = \sum_{k} \exp(-\beta \varepsilon_{k})$$
$$= \frac{V}{(2\pi)^{3}} \int d\mathbf{k} \exp(-\beta \varepsilon_{k})$$
$$= \frac{V}{(2\pi)^{3}} \int_{0}^{\infty} 4\pi k^{2} d\mathbf{k} \exp(-\frac{\beta \hbar^{2} k^{2}}{2m})$$
$$= \frac{V}{2\pi^{2}} \sqrt{\frac{\pi}{2}} \frac{1}{\hbar^{3}} \left(\frac{m}{\beta}\right)^{3/2}$$
$$= V \left(\frac{mk_{B}T}{2\pi\hbar^{2}}\right)$$

© N particle system (identical case)

$$Z_{C}(\beta) = \frac{1}{N!} [Z_{C1}(\beta)]^{N}$$
$$= \frac{V^{N}}{N!} [\frac{1}{2\pi^{2}} \sqrt{\frac{\pi}{2}} (\frac{m}{\hbar^{2}\beta})^{3/2}]^{N}$$
$$= \frac{V^{N}}{N!} (\frac{m}{2\pi\hbar^{2}\beta})^{3N/2}$$
$$= \frac{V^{N}}{N!} (\frac{mk_{B}T}{2\pi\hbar^{2}})^{3N/2}$$
$$= \frac{V^{N}}{N!} (\frac{2\pi mk_{B}T}{\hbar^{2}})^{3N/2}$$

Note that

$$\frac{1}{2\pi^2}\sqrt{\frac{\pi}{2}} = \sqrt{\frac{1}{8\pi^3}} = \frac{1}{(2\pi)^{3/2}}, \qquad \hbar = \frac{h}{2\pi}$$

The Helmholtz free energy:

$$F = -k_{B}T \ln Z_{C}(\beta, T, V)$$

$$= -k_{B}T[N \ln V - \ln N! + \frac{3N}{2} \ln T + \frac{3N}{2} \ln(\frac{2\pi m k_{B}}{h^{2}})]$$

$$= -k_{B}T[N \ln V - N \ln N + N + \frac{3N}{2} \ln T + \frac{3N}{2} \ln(\frac{2\pi m k_{B}}{h^{2}})]$$

$$= -Nk_{B}T[\ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln T + 1 + \frac{3}{2} \ln(\frac{2\pi m k_{B}}{h^{2}})]$$

or

$$F = -Nk_{B}T\left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + 1 + \frac{3}{2}\ln\left(\frac{2\pi mk_{B}}{h^{2}}\right)\right]$$

 $\ln Z_{C}(\beta, T, V)$ is obtained as

$$\ln Z_{C}(\beta, T, V) = N[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + 1 + \frac{3}{2}\ln(\frac{2\pi mk_{B}}{h^{2}})]$$

The average energy

$$E = -T^{2} \frac{\partial}{\partial T} \left(\frac{F}{T}\right)_{V}$$
$$= k_{B}T^{2} \left(\frac{\partial}{\partial T} \ln Z\right)_{V}$$
$$= -\left(\frac{\partial}{\partial \beta} \ln Z\right)_{V}$$
$$= \frac{3}{2}Nk_{B}T$$

$$E = \frac{3}{2} N k_B T$$

The heat capacity at constant volume:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}Nk_B$$

For $N = N_A$, we have $C_V = \frac{3}{2}R$, where R is the gas constant. The heat capacity at constant pressure is

$$C_P = Cv + R = \frac{5}{2}R$$
, (Mayer's relation)

The entropy S is

$$S = \frac{E - F}{T}$$

= $\frac{3}{2}Nk_B + Nk_B [\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + 1 + \frac{3}{2}\ln(\frac{2\pi nk_B}{h^2})]$
= $Nk_B [\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln(\frac{2\pi nk_B T}{h^2}) + \frac{5}{2}]$

or

$$S = Nk_B \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi nk_B T}{h^2}\right) + \frac{5}{2} \right]$$

(Sackur–Tetrode equation)

The pressure P is

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_B T}{V}$$

$$PV = Nk_BT$$

8. Gibbs paradox (revisited)

We need to use the Sackur-Tetrode equation for the identical gases

$$S = Nk_{B}\left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln(T) + C\right]$$

where C is a constant, and $N = nN_A$





Fig. The initial state before mixing and the final state after mixing.

The entropy in the initial state before the mixing

$$\begin{split} S_i &= n_1 R [\ln \left(\frac{V_1}{n_1 N_A}\right) + \frac{3}{2} \ln(T) + C] \\ &+ n_2 R [\ln \left(\frac{V_2}{n_2 N_A}\right) + \frac{3}{2} \ln(T) + C] \\ &= n_1 R [\ln \left(\frac{RT}{P N_A}\right) + \frac{3}{2} \ln(T) + C] \\ &+ n_2 R [\ln \left(\frac{RT}{P N_A}\right) + \frac{3}{2} \ln(T) + C] \\ &= (n_1 + n_2) R [\ln \left(\frac{k_B T}{P}\right) + \frac{3}{2} \ln(T) + C] \end{split}$$

since $PV_1 = n_1 RT$ and $PV_2 = n_2 RT$

$$S_i = n_1 R[\ln\left(\frac{V_1}{n_1 N_A}\right) + \frac{3}{2}\ln(T)] + C$$

The entropy in the final state after the mixing is

$$S_{f} = (n_{1} + n_{2})R[\ln\left(\frac{V_{1} + V_{2}}{(n_{1} + n_{2})N_{A}}\right) + \frac{3}{2}\ln(T) + C]$$
$$= (n_{1} + n_{2})R[\ln\left(\frac{RT}{PN_{A}}\right) + \frac{3}{2}\ln(T) + C]$$
$$= (n_{1} + n_{2})R[\ln\left(\frac{k_{B}T}{P}\right) + \frac{3}{2}\ln(T) + C]$$

since $P(V_1 + V_2) = (n_1 + n_2)RT$.

So we have

$$S_i = S_f$$
.

The Gibbs paradox is no longer a paradox.

9. Problem and solution (I)

K. Huang Introduction to Statistical mechanics ((Problem 3-6))

3.6 A mixture of two ideal gases undergoes an adiabatic transformation. The gases are labeled 1,2. Their densities and heat capacities are denoted by n_{j} , C_{Vj} , $C_{Pj}(j = 1, 2)$. Show that the pressure *P* and volume *V* of the system obey the constraint PV^{ξ} = constant, where

$$\xi = \frac{n_1 C_{P1} + n_2 C_{P2}}{n_1 C_{V1} + n_2 C_{V2}}$$

Hint. The entropy of the system does not change, but those of the components do. For the entropy change of an ideal gas, use $\Delta S = Nk \ln[(V_f / V_i)(T_f / T_i)^{3/2}]$, where *f* and *i* denote final and initial values.

((Solution))

$$dU = TdS - PdV = nC_V dT$$

$$dS = \frac{P}{T}dV + \frac{nC_V}{T}dT = Nk_B\frac{dV}{V} + \frac{nC_V}{T}dT$$

$$S = Nk_B \ln V + nC_V \ln T = n(R \ln V + C_V \ln T)$$

Using this equation

$$\Delta S = \Delta S_1 + \Delta S_2$$

= $[n_1 R \ln(\frac{V_f}{V_i}) + n_1 C_{V1} \ln \frac{T_f}{T_i}] + [n_2 R \ln(\frac{V_f}{V_i}) + n_1 C_{V1} \ln \frac{T_f}{T_i}]$
= $(n_1 + n_2) R \ln\left(\frac{V_f}{V_i}\right) + (n_1 C_{V1} + n_2 C_{V2}) \ln \frac{T_f}{T_1} = 0$

$$\frac{(n_1 + n_2)R}{(n_1C_{V1} + n_2C_{V2})} \ln\left(\frac{V_f}{V_i}\right) + \ln\frac{T_f}{T_1} = 0$$

or

$$\ln\frac{T_f}{T_i} + \zeta \ln\left(\frac{V_f}{V_i}\right) = 0$$

where

$$\varsigma = \frac{(n_1 + n_2)R}{(n_1 C_{V1} + n_2 C_{V2})}$$

or

$$TV^{\varsigma} = \text{constant}$$

Putting $PV = nRT = (n_1 + n_2)RT$

 $PV^{\xi} = \text{constant}$

where

$$\begin{split} \xi &= 1 + \varsigma \\ &= 1 + \frac{(n_1 + n_2)R}{(n_1 C_{V1} + n_2 C_{V2})} \\ &= \frac{(n_1 + n_2)R + (n_1 C_{V1} + n_2 C_{V2})}{n_1 C_{V1} + n_2 C_{V2}} \\ &= \frac{n_1 C_{P1} + n_2 C_{P2}}{n_1 C_{V1} + n_2 C_{V2}} \end{split}$$

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