Lecture 4: The First and the Second Laws of the Thermodynamics

本章的目的是要介紹熱力學第一定律與第二定律。同時也將從不同的角度切入，去了解熱力學中熵值（entropy）的定義與意義。

4.1. The first law of the thermodynamics

一個分布函數為 $f(\mathbf{x},\mathbf{v},t)$ 的氣體系統，“單位體積”內氣體的總動能為

$$\iiint \frac{1}{2} m v^2 f(\mathbf{x},\mathbf{v},t) d^3 v = \frac{1}{2}\rho V^2 + \frac{3}{2} p$$

證明：

$$\iiint \frac{1}{2} m v^2 f(\mathbf{x},\mathbf{v},t) d^3 v$$

$$= \iiint \frac{1}{2} m[(\mathbf{v}-\mathbf{V})+\mathbf{V}]\cdot[(\mathbf{v}-\mathbf{V})+\mathbf{V}] f(\mathbf{x},\mathbf{v},t) d^3 v$$

$$= \frac{1}{2}\mathbf{V}\cdot\mathbf{V}\iiint m f(\mathbf{x},\mathbf{v},t) d^3 v + \iiint \frac{1}{2} m(\mathbf{v}-\mathbf{V})\cdot(\mathbf{v}-\mathbf{V}) f(\mathbf{x},\mathbf{v},t) d^3 v$$

$$= \frac{1}{2}\rho V^2 + \frac{3}{2} p$$

其中這個氣塊之平均速度所對應的動能是

$$\frac{1}{2}\mathbf{V}\cdot\mathbf{V}\iiint m f(\mathbf{x},\mathbf{v},t) d^3 v = \frac{1}{2}\rho V^2$$

這個氣塊內氣體熱速度所對應的動能是

$$\iiint \frac{1}{2} m(\mathbf{v}-\mathbf{V})\cdot(\mathbf{v}-\mathbf{V}) f(\mathbf{x},\mathbf{v},t) d^3 v = \frac{3}{2} p$$

若將氣塊內氣體熱速度所對應的動能看成是此氣體的一種內能，則此氣塊中“單位體積”的內能（internal energy）就是

$$\frac{U}{Vol.} = \frac{3}{2} p \tag{4.1}$$

若此氣體為理想氣體，則會滿足理想氣體方程式

$$p = n k_B T \tag{4.2}$$

其中 n 表示個數密度， k_B 表示 Boltzmann's constant， p 表示氣體熱壓，T 表示氣體溫度（單位為絕對溫度）。現在，若考慮一個傳統熱力學、機械熱力學所常常面對的「密閉容器」：體積為 $Vol.$ 的氣體中有固定之 N 個氣體粒子，故個數密度滿足

$$nVol. = N = \text{constant} \quad (4.3)$$

因此，理想氣體方程式(4.2) 可改寫為

$$pVol. = Nk_BT \quad (4.4)$$

氣體的內能可改寫為

$$U = \frac{3}{2}Nk_BT \quad (4.5)$$

也就是說，理想氣體的內能“只是溫度的函數”。

早期的科學家更進一步由實驗發現加熱與壓縮做功可以提高氣體溫度，因此可以增加氣體內能，也就是

$$\Delta U = \delta Q_{in} + \delta W \quad (4.6)$$

其中 δQ_{in} 表示流入的熱，$\delta Q_{in} > 0$ 表示熱加入系統，$\delta Q_{in} < 0$ 表示熱散出去；δW 表示壓縮做功，也就是

$$\delta W = -p\Delta Vol. \quad (4.7)$$

其中 $\Delta Vol.$表示體積的體積變化，$\Delta Vol. > 0$ 表示體積增加，$\Delta Vol. < 0$ 表示體積減少。因為壓縮氣體可以增加氣體溫度，所以 $p\Delta Vol.$前面為負號，表示壓縮做功。

註 1：壓縮氣體代表“做功”，我們可以用 x 方向的力所做的功當作範例來了解壓縮氣體的“做功”過程。

$$Work = (F_x\hat{x})\cdot(\Delta x\hat{x}) = p(\Delta y\Delta z\hat{x})\cdot(\Delta x\hat{x}) = p\Delta x\Delta y\Delta z = p\Delta Vol.$$

註 2：方程式(4.6)式，就是所謂的熱力學第一定律。其實“熱力學第一定律”就是能量守恆定律。之所以會取另一個名字，這是因為早期科學家對熱的意義，不甚了解之故。

Exercise 4.1. Show that

$$\delta Q_{in} = C_V T\frac{\Delta p}{p} + C_P T\frac{\Delta Vol.}{Vol.}$$

where $C_V = (3/2)Nk_B$ is the heat capacity at constant volume （等容熱容）,

$C_P = (5/2)Nk_B$ is the heat capacity at constant pressure （等壓熱容）.

Proof:

Equation (4.1) yields

$$U = \frac{3}{2}pVol. \quad (4.8)$$

Substituting equation (4.8) into equation (4.6) to eliminate U, and substituting equation (4.7) into equation (4.6) to eliminate δW, it yields

$$\frac{3}{2}\Delta(pVol.) = \delta Q_{in} - p\Delta Vol. \tag{4.9}$$

Since $\Delta(pVol.) = Vol.\Delta p + p\Delta Vol.$, equation (4.9) can be rewritten as

$$\delta Q_{in} = \frac{3}{2}Vol.\Delta p + \frac{5}{2}p\Delta Vol. \tag{4.10}$$

Equation (4.10) can be rewritten as

$$\delta Q_{in} = \frac{3}{2}(pVol.)\frac{\Delta p}{p} + \frac{5}{2}(pVol.)\frac{\Delta Vol.}{Vol.} \tag{4.11}$$

Substituting equation (4.4) into equation (4.11), it yields

$$\delta Q_{in} = \frac{3}{2}Nk_B T\frac{\Delta p}{p} + \frac{5}{2}Nk_B T\frac{\Delta Vol.}{Vol.} \tag{4.12}$$

For constant volume, equation (4.12) becomes

$$\delta Q_{in}\Big|_{Vol.} = C_V T\frac{\Delta p}{p}\Big|_{Vol.} \tag{4.13}$$

where $C_V = (3/2)Nk_B$ is the heat capacity at constant volume（等容熱容）.

For constant pressure, equation (4.12) becomes

$$\delta Q_{in} = C_P T\frac{\Delta Vol.}{Vol.} \tag{4.14}$$

where $C_P = (5/2)Nk_B$ is the heat capacity at constant pressure（等壓熱容）.

Substituting the definition of C_V and C_P in to equation (4.12), it yields

$$\delta Q_{in} = C_V T\frac{\Delta p}{p} + C_P T\frac{\Delta Vol.}{Vol.} \tag{4.15}$$

Equation (4.15) can be rewritten as

$$\delta Q_{in} = C_V T\Delta\ln(pVol.^{\gamma}) \tag{4.16}$$

where ratio of the specific heats (比熱比) is

$$\gamma = C_P / C_V = 5/3 \tag{4.17}$$

By definition $N = nV$, thus equation (4.12) can be rewritten as

$$\delta Q_{in} = \frac{3}{2}Nk_B T(\frac{\Delta p}{p} - \frac{5}{3}\frac{m\Delta n}{mn}) = \frac{3}{2}Nk_B T\Delta\ln(p\rho^{-5/3}) = C_V T\Delta\ln(p\rho^{-\gamma}) \tag{4.18}$$

where mass density $\rho = mn$.

註：如果氣體的自由度不是 3，而是 f ，則以上這些熱力學方程式應該改為

$$U = \frac{f}{2} N k_B T \tag{4.5a}$$

Substituting equation (4.4) into equation (4.5a), it yields

$$U = \frac{f}{2} pVol. \tag{4.8a}$$

Substituting equation (4.8a) into equation (4.6) to eliminate U, and substituting equation (4.7) into equation (4.6) to eliminate δW , it yields

$$\frac{f}{2}\Delta(pVol.) = \delta Q_{in} - p\Delta Vol. \tag{4.9a}$$

Since $\Delta(pVol.) = Vol.\Delta p + p\Delta Vol.$, equation (4.9a) can be rewritten as

$$\delta Q_{in} = \frac{f}{2} Vol.\Delta p + (\frac{f}{2}+1) p\Delta Vol. \tag{4.10a}$$

Equation (4.10a) can be rewritten as

$$\delta Q_{in} = \frac{f}{2}(pVol.)\frac{\Delta p}{p} + \frac{f+2}{2}(pVol.)\frac{\Delta Vol.}{Vol.} \tag{4.11a}$$

Substituting equation (4.4) into equation (4.11a), it yields

$$\delta Q_{in} = \frac{f}{2} N k_B T \frac{\Delta p}{p} + \frac{f+2}{2} N k_B T \frac{\Delta Vol.}{Vol.} \tag{4.12a}$$

Thus, equation (4.12a) can be rewritten as

$$\delta Q_{in} = C_V T \frac{\Delta p}{p} + C_P T \frac{\Delta Vol.}{Vol.} \tag{4.15a}$$

where $C_V = (f/2) N k_B$ is the heat capacity at constant volume （等容熱容）and $C_P = (f+2) N k_B / 2$ is the heat capacity at constant pressure （等壓熱容）.

Equation (4.15a) can be rewritten as

$$\delta Q_{in} = \frac{f}{2} N k_B T \Delta \ln(pVol.^{(f+2)/f}) = C_V T \Delta \ln(pVol.^{\gamma}) \tag{4.16a}$$

where the ratio of the specific heats (比熱比) is

$$\gamma = C_P / C_V = (f+2)/f \tag{4.17a}$$

By definition $N = nV$, thus equation (4.12a) can be rewritten as

$$\delta Q_{in} = \frac{f}{2} N k_B T (\frac{\Delta p}{p} - \frac{f+2}{f}\frac{m\Delta n}{mn}) = \frac{f}{2} N k_B T \Delta \ln(p\rho^{-(f+2)/f}) = C_V T \Delta \ln(p\rho^{-\gamma}) \tag{4.18a}$$

4.2. Entropy

早期的科學家由實驗發現，如果快速改變氣體的體積（壓縮或膨脹），讓系統與外界來不及進行熱交換（但整個過程，熱壓力可以改變，溫度也可以改變），則有一個物理量會守恆。那就是熵（entropy）。科學家利用實驗定義 熵（entropy）的變化量（ΔS）為

$$\Delta S = \frac{\delta Q_{in}}{T} \tag{4.19}$$

Substituting equation (4.16) into equation (4.19) to eliminate δQ_{in}, it yields

$$\Delta S = C_V \Delta \ln(pVol.^{\gamma}) \tag{4.20}$$

Substituting equation (4.18) into equation (4.19) to eliminate δQ_{in}, it yields

$$\Delta S = \frac{3}{2} N k_B \Delta \ln(p\rho^{-5/3}) \tag{4.21}$$

由方程式(4.21)我們可以定義理想氣體的熵（entropy）為

$$S = \frac{3}{2} N k_B \ln(p\rho^{-5/3}) + S_0 = C_V \ln(p\rho^{-\gamma}) + S_0 \tag{4.22}$$

因此在絕熱過程中，理想氣體有一個絕熱物理不變量：

$$\ln(p\rho^{-\gamma}) = \text{constant}. \tag{4.23}$$

我們也可以將(4.19)式代入熱力學第一定律(4.6)式，消去熱流δQ_{in} ，將(4.7)式代入(4.6)式消去δW 得

$$\Delta U = T\Delta S - p\Delta Vol. \tag{4.24}$$

式(4.24)是“熱力學第一定律”的另一種形式。根據內能的定義 $U = (3/2)Nk_B T$ ，式(4.24)可再改寫為

$$\frac{3}{2} N k_B \Delta T = T\Delta S - p\Delta Vol. \tag{4.25}$$

其中最後一項壓力與體積也可用T 與 S來表示之，

$$p(T,S) = (Nk_B T)^{5/2} \exp(-\frac{S - S_0}{Nk_B}) \tag{4.26a}$$

$$Vol.(T,S) = (Nk_B T)^{-(3/2)} \exp(\frac{S - S_0}{Nk_B}) \tag{4.26b}$$

這些熱力學方程式，原來都是由實驗結果所歸納出來的經驗式。我們可以對照上一章所推導出來的能量方程式，來了解這些經驗式中，每一項所內涵的物理意義。

4.3. Thermodynamic processes and thermodynamic cycles

方程式(4.3)~(4.7), (4.19)一共有六組 independent equations。但是 unknowns 未知數卻有八個。這八個未知數包括了 U, δQ_{in}, δW, T, S, p, n, and $Vol.$ 。因此六組方程式只能將 unknowns 的自由度由 8 降到 2。此外，值得一提的是，八個未知數中δQ_{in}, δW不屬於氣體的狀態變數（state variables），而是造成氣體狀態改變的過程變數（process variables）。其他六個變數U, T, S, p, n, and $Vol.$，都是描述氣體狀態的狀態變數。在傳統的熱力學中，我們常選用的「兩個一組」的自由變數（free parameters or independent variables）為（p,$Vol.$）或（T, S），如 Table 1 第一橫列所示。

在 Table 1 第二橫列中，我們可以看到變數變換的過程。也就是說，如果考慮 independent variables 為（p,$Vol.$），則我們可以把T, S都寫成是（p,$Vol.$）的函數。反之，如果考慮 independent variables 為（T, S），則可以把p,$Vol.$都寫成是（T, S）的函數。如果我們再加上一組條件，則自由變數就只剩一個了，於是我們可以在（p,$Vol.$）空間中或（T, S）空間中，畫出一條曲線。在 Table 1 第三到六橫列中列出了四種常見的熱力過程（條件），以及在這些條件下，如何估算δQ_{in}, δW, and ΔU。這四種常見的熱力過程依次為：（一）快速壓縮或膨脹時所呈現的等熵或絕熱過程($\Delta S = 0$ or $\delta Q_{in} = 0$)（二）緩慢壓縮或膨脹時所呈現的等溫過程($\Delta T = 0$)（三）等壓過程($\Delta p = 0$)（四）等容過程($\Delta Vol. = 0$)。將這些熱力過程適當的組合，機械工程師設計出一些理論與實用的熱機（heat engine）與冷機（refrigerator or air condition）。這些引擎運轉的過程通稱為 thermodynamic cycle 熱力循環。科學家發現，冷機必須做功才可能將熱（heat）由低溫處傳輸到高溫處。而熱機引擎也不可能將它所吸收的熱全部用來做功而不散熱。因此引擎運轉久了所生的熱，將會降低引擎的工作效率 efficiency。

Exercise 4.2.

Use google to find the following thermodynamic cycles and sketch these cycles on the pressure-volume diagram (p-$Vol.$-diagram) and on the temperature-entropy diagram (T-S-diagram). On these diagram, please indicate the heat flow direction, and estimate the work done by the engine.

(i) Carnot cycle	(ii) Otto cycle	(iii) Diesel cycle
(iv) Brayton cycle (or Joule cycle)	(v) Rankine cycle (a steam engine)	

Table 1. Thermodynamic coordinates and thermodynamic processes

Independent Variables	p and $Vol.$	T and S
coordinate transform	$S(p,Vol.) = \frac{3}{2}Nk_B \ln(pVol.^{5/3}) + S_0$ $T(p,Vol.) = \frac{pVol.}{Nk_B}$	$p(T,S) = (Nk_BT)^{5/2}\exp(-\frac{S-S_0}{Nk_B})$ $Vol.(T,S) = (Nk_BT)^{-(3/2)}\exp(\frac{S-S_0}{Nk_B})$
$\Delta S = 0$	$\delta Q_{in} = 0$ $\Delta U = \frac{3}{2}Nk_B\Delta T$ $\delta W = \Delta U$ or (Note 1)	$\delta Q_{in} = 0$ $\Delta U = \frac{3}{2}Nk_B\Delta T = \frac{3}{2}Nk_B(T_f - T_i)$ $\delta W = \Delta U$
$\Delta T = 0$	$\Delta U = 0$ (Note 2) $\delta W = -Nk_BT\ln\frac{(Vol.)_f}{(Vol.)_i}$ $\delta Q_{in} = Nk_BT\ln\frac{(Vol.)_f}{(Vol.)_i}$	$\Delta U = 0$ $\delta Q_{in} = T\Delta S = T(S_f - S_i)$ $\delta W = -\Delta Q_{in}$
$\Delta p = 0$	$\Delta U = \frac{3}{2}\Delta[p(Vol.)] = \frac{3}{2}p\Delta Vol.$ $\delta W = -p\Delta Vol.$ $\delta Q_{in} = \Delta U - \delta W = \frac{5}{2}p\Delta Vol.$ or (Note-3)	$\Delta U = \frac{3}{2}\Delta[p(Vol.)] = \frac{3}{2}p\Delta Vol.$ $\delta W = -p\Delta Vol.$ $\delta Q_{in} = \Delta U - \delta W = \frac{5}{2}p\Delta Vol.$ or (Note-3)
$\Delta Vol. = 0$	$\delta W = 0$ $\Delta U = \frac{3}{2}\Delta[p(Vol.)] = \frac{3}{2}Vol.\Delta p$ $\delta Q_{in} = \Delta U - \delta W = \frac{3}{2}Vol.\Delta p$ or (Note-4)	$\delta W = 0$ $\Delta U = \frac{3}{2}\Delta[p(Vol.)] = \frac{3}{2}Vol.\Delta p$ $\delta Q_{in} = \Delta U - \delta W = \frac{3}{2}Vol.\Delta p$ or (Note-4)

Note-1:

Since

$$Vol.(T,S) = (Nk_BT)^{-(3/2)}\exp(\frac{S-S_0}{Nk_B})$$

it yields

$$\frac{dVol.}{Vol.} = -\frac{3}{2}\frac{dT}{T} + \frac{dS}{Nk_B}$$

For $\Delta S = 0$ it yields

$$\delta W = -\int p\,dVol. = +\frac{3}{2}\int p\frac{Vol.}{T}dT = \frac{3}{2}Nk_B\int dT = \frac{3}{2}Nk_B\Delta T$$

Note-2:

For $\Delta T = 0$ it yields

$$\delta W = -\int p\,dVol. = -\int p\frac{Vol.}{Nk_B}dS = -T\int dS = -T\Delta S$$

or

$$\delta W = -\int p\,dVol. = -\int \frac{Nk_BT}{Vol.}dVol. = -Nk_BT\ln\frac{(Vol.)_f}{(Vol.)_i}$$

$$\delta Q_{in} = \int T\,dS = T\int dS = T\int Nk_B\frac{dVol.}{Vol.} = Nk_BT\ln\frac{(Vol.)_f}{(Vol.)_i}$$

Note-3: For $\Delta p = 0$

$$\frac{dVol.}{Vol.} = -\frac{3}{2}\frac{dT}{T} + \frac{dS}{Nk_B}$$

$$\delta Q_{in} = \int T\,dS = \int TC_V\,d\ln[p(Vol.)^{C_P/C_V}] = \int TC_V\frac{C_P}{C_V}\frac{dVol.}{Vol.} = \int_{Vol._0}^{Vol._0+\Delta Vol.}C_P\frac{p}{Nk_B}dVol. = \frac{5}{2}p\Delta Vol.$$

Note-4: For $\Delta Vol. = 0$

$$\delta Q_{in} = \int T\,dS = \int TC_V\,d\ln[p(Vol.)^{C_P/C_V}] = \int TC_V\frac{dp}{p} = \int_{p_0}^{p_0+\Delta p}C_V\frac{Vol.}{Nk_B}dp = \frac{3}{2}Vol.\Delta p$$

4.3.1. Efficiency of a heat engine:

Let Q_H be the heat flow added into the engine from a hot reservoir with temperature T_H.

Let Q_C be the heat flow released from the engine into a cold reservoir with temperature T_C.

Let W be the work done by the engine.

The thermodynamic cycle of a heat engine concerts the input heat flux Q_H into work W but also release heat flux Q_C into the environment. The process can be denoted as

$$Q_H \Rightarrow Q_C + W$$

The efficiency of the heat engine is defined by the ratio benefit/cost, which is equal to

$$e_E = W / Q_H$$

For heat engine, $Q_H / T_H \le Q_C / T_C$, it yields

$$e_E = W / Q_H = (Q_H - Q_C)/Q_H = 1 - (Q_C / Q_H) \le 1 - (T_C / T_H)$$

Exercise 4.3.

Show that for Carnot-cycle heat engine $e_E = 1 - (T_C / T_H)$

Proof:

Let us consider a Carnot cycle, $a \to b \to c \to d \to a$ with total work W done by the Carnot cycle, where the different thermodynamic states are characterized by

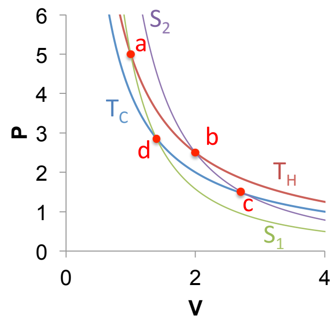
thermodynamic state a: $T = T_H$, $S = S_1$

thermodynamic state b: $T = T_H$, $S = S_2$

thermodynamic state c: $T = T_C$, $S = S_2$

thermodynamic state d: $T = T_C$, $S = S_1$

with $T_H > T_C$ and $S_2 > S_1$.



The total work done by the Carnot cycle can be evaluated from

$$W = \oint P\,dVol. = \int_a^b P\,dVol. + \int_b^c P\,dVol. + \int_c^d P\,dVol. + \int_d^a P\,dVol.$$

For the isothermal expansion process ($a \to b$), there is no change on the internal energy. Thus, the work output to the environment is equal to the input of heat flow Q_H. That is

$$\int_a^b P\,dVol. = Q_H = (S_2 - S_1)T_H$$

Likewise, for the isothermal compression process ($c \to d$) the work output to the environment is negative with magnitude equal to the release of heat flow Q_C. That is

$$\int_c^d P\,dVol. = -Q_C = (S_1 - S_2)T_C$$

During the isentropic expansion process ($b \to c$) the work output to the environment is achieved by reducing the internal energy of the engine system. That is,

$$\int_b^c P\,dVol. = \frac{3}{2} N k_B (T_H - T_C)$$

During the isentropic compression process ($d \to a$), the negative work output to the environment will result in increasing of the internal energy of the engine system. That is,

$$\int_d^a P\,dVol. = -\frac{3}{2} N k_B (T_H - T_C)$$

Thus, we have

$$\int_b^c P\,dVol. + \int_d^a P\,dVol. = 0$$

Therefore, the total work done by the Carnot cycle is $W = \oint P\,dVol. = Q_H - Q_C$

As a result, the efficiency of the Carnot-cycle heat engine is equal to

$$e_E = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{(S_2 - S_1)T_C}{(S_2 - S_1)T_H} = 1 - \frac{T_C}{T_H}$$

4.3.2. Efficiency of a refrigerator:

Let Q_C be the heat flow extracted by the refrigerator from a cool reservoir with temperature T_C.

Let Q_H be the heat flow released from the refrigerator into the hot reservoir with temperature T_H.

Let W be the input power to run the refrigerator.

The thermodynamic cycle of a refrigerator yields

$$Q_C + W \Rightarrow Q_H$$

The efficiency of the refrigerator equal to

$$e_R = Q_C / W$$

For refrigerator, $Q_H / T_H \geq Q_C / T_C$, it yields

$$e_E = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} = \frac{1}{(Q_H / Q_C) - 1} \leq \frac{1}{(T_H / T_C) - 1}$$

Again, the Carnot-cycle refrigerator has the best efficiency, which is equal to

$$e_E = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} = \frac{1}{(Q_H / Q_C) - 1} = \frac{1}{(T_H / T_C) - 1}$$

4.4. Definition of entropy in the statistic thermodynamics

Let us consider a distribution function similar to the one discussed in equation (2.22), i.e., an equilibrium ($\partial / \partial t = 0$), uniform ($\partial / \partial x = \partial / \partial y = \partial / \partial z = 0$), and normal distribution in the velocity space,

$$f(v_x, v_y, v_z) = \frac{n}{(\sqrt{2\pi}\sigma)^3} \exp(-\frac{(v_x - V_x)^2 + (v_y - V_y)^2 + (v_z - V_z)^2}{2\sigma^2}) \tag{4.27}$$

where

$$n = \iiint f(\mathbf{v}) d^3 v \tag{4.28}$$

is the number density,

$$\mathbf{V} = \frac{1}{n} \iiint \mathbf{v} f(\mathbf{v}) d^3 v \tag{4.29}$$

is the average velocity, $\mathbf{V} = \mathbf{e}_x V_x + \mathbf{e}_y V_y + \mathbf{e}_z V_z$, and

$$\sigma^2 = k_B T / m = \frac{1}{n} \iiint (v_x - V_x)^2 f(\mathbf{v}) d^3 v = \frac{1}{n} \iiint (v_y - V_y)^2 f(\mathbf{v}) d^3 v = \frac{1}{n} \iiint (v_z - V_z)^2 f(\mathbf{v}) d^3 v \tag{4.30}$$

is the variance of the distribution function in each velocity component. Let us consider the following integration

$$I = \iiint f (\ln f) d^3 v \tag{4.31}$$

where

$$\ln f = [\ln n - \frac{3}{2} \ln(2\pi) - 3 \ln \sigma] - \frac{(v_x - V_x)^2 + (v_y - V_y)^2 + (v_z - V_z)^2}{2\sigma^2} \tag{4.32}$$

Substituting (4.32) into (4.31), it yields

$$\begin{aligned} I &= \iiint f [(\ln n - \frac{3}{2} \ln(2\pi) - 3 \ln \sigma) - \frac{(v_x - V_x)^2 + (v_y - V_y)^2 + (v_z - V_z)^2}{2\sigma^2}] d^3 v \\ &= n(\ln n - \frac{3}{2} \ln(2\pi) - 3 \ln \sigma) - \frac{1}{2\sigma^2} \iiint f [(v_x - V_x)^2 + (v_y - V_y)^2 + (v_z - V_z)^2] d^3 v \end{aligned} \tag{4.33}$$

Substituting equation (4.30) into equation (4.33), it yields

$$I = n(\ln n - \frac{3}{2}\ln(2\pi) - 3\ln\sigma) - \frac{3n\sigma^2}{2\sigma^2}$$
$$= n(\ln n - \frac{3}{2}\ln(2\pi) - 3\ln\sigma) - \frac{3n}{2}$$
$$= -n[3\ln\sigma - \ln n + \frac{3}{2}\ln(2\pi) + \frac{3}{2}]$$
$$= -n[3\ln\sqrt{\frac{k_B T}{m}} - \ln(n) + \frac{3}{2}\ln(2\pi) + \frac{3}{2}]$$
$$= -n[3\ln\sqrt{\frac{nk_B T}{nm}} - \ln(mn) + \ln(m) + \frac{3}{2}\ln(2\pi) + \frac{3}{2}]$$
$$= -n[\frac{3}{2}\ln\frac{p}{\rho} - \ln\rho + \ln(m) + \frac{3}{2}\ln(2\pi) + \frac{3}{2}]$$
$$= \frac{-N}{Vol.}[\frac{3}{2}\ln(p\rho^{-5/3}) + \ln(m) + \frac{3}{2}\ln(2\pi) + \frac{3}{2}]$$

Namely,

$$I = \iiint f(\ln f)d^3v = \frac{-N}{Vol.}[\frac{3}{2}\ln(p\rho^{-5/3}) + \ln(m) + \frac{3}{2}\ln(2\pi) + \frac{3}{2}] \tag{4.34}$$

If we define the entropy density (i.e., entropy per unit volume) to be

$$s = -k_B\iiint f(\ln f)d^3v \tag{4.35}$$

Equations (4.27)~(4.34) and (4.35) yields, for an equilibrium ($\partial/\partial t = 0$), spatially uniform ($\partial/\partial x = \partial/\partial y = \partial/\partial z = 0$), and isotropic distribution in the velocity space, the entropy density is reduce to

$$s = -k_B\iiint f(\ln f)d^3v = \frac{(3/2)Nk_B\ln(p\rho^{-5/3})}{Vol.} + \frac{\text{constant}}{Vol.}$$

where the constant $= (3Nk_B/2)\ln(2\pi m) + (Nk_B/2)$

For spatially uniform distribution, the entropy density is also uniform in space. So the entropy in a volume $Vol.$ is

$$S = s(Vol.) = -k_B(Vol.)\iiint f(\ln f)d^3v = \frac{3}{2}Nk_B\ln(p\rho^{-5/3}) + \text{constant} \tag{4.36}$$

The equation (4.36) is the same as the equation (4.23), except the integration constant. For non-uniform and/or non-isotropic system, we can generalize the definition of entropy function in a volume $Vol.$ to be

$$S = -k_B\iiint_{Vol.}[\iiint f(\ln f)d^3v]d^3x \tag{4.37}$$

or simply use the entropy density s to define the entropy. Let $s = nS$. Equation (4.35) yields

$$S = \frac{s}{n} = -\frac{k_B}{n}\iiint f(\ln f)d^3v \tag{4.38}$$

If we define $\log w = -\ln f$, and

$$\log W = \iiint_{Vol.}[\iiint f(\ln w)d^3v]d^3x = -\iiint_{Vol.}[\iiint f(\ln f)d^3v]d^3x \tag{4.39}$$

then the entropy function can be written as

$$S = k_B \log W \tag{4.40}$$

4.5. The second law of the thermodynamics

這節中，我們將由傳統熱力學、流體力學、統計熱力等三個不同的方向，介紹熱力學第二定律。早期的科學家經過實驗發現，一個封閉系統的熵值隨時間的變化，為零或大於零 ($\Delta S \geq 0$)。這就是熱力學第二定律。既然是實驗結果，就不要問為什麼！以下我們將從流體力學與統計熱力來看為什麼 $\Delta S \geq 0$ 。

4.5.1. 由流體力學看熱力學第二定律

第 α 種流體的能量方程式（詳見 Lecture 3），可以改寫為

$$\frac{3}{2}(\frac{\partial}{\partial t} + \mathbf{V}_\alpha \cdot \nabla)[\ln(p_\alpha \rho_\alpha^{-5/3})] = -\frac{\nabla \cdot \mathbf{q}_\alpha + (\mathbf{\Pi}_\alpha \cdot \nabla) \cdot \mathbf{V}_\alpha}{p_\alpha} + \frac{\text{external energy input per unit volume}}{p_\alpha} \tag{3.25a}$$

如果為一個封閉的系統 $\nabla \cdot \mathbf{q}_\alpha = 0$ 也沒有 external energy input，則

$$\frac{3}{2}(\frac{\partial}{\partial t} + \mathbf{V}_\alpha \cdot \nabla)[\ln(p_\alpha \rho_\alpha^{-5/3})] = -\frac{(\mathbf{\Pi}_\alpha \cdot \nabla) \cdot \mathbf{V}_\alpha}{p_\alpha} \tag{4.41}$$

其中剪壓(stress tensor) 隨時間改變的情形，可以由“壓力方程式” (the pressure equation of the αth species)求得。而壓力方程式是可由(3.5) 式左右兩邊各乘以 $m_\alpha \mathbf{vv}$ ，再加上考慮外力造成的剪壓變化，求得。因為計算繁複，請參考參考文獻 Rossi & Olbert (1970) 以及 Lyu (2010) 中詳細的推導。總之，根據壓力方程式、連續方程式、動量方程式，我們可以證明古典力學（例如：Symon, 1971）中，所估算的剪壓形式是一個不錯的近似形式。

古典力學（例如：Symon, 1971）中，估算剪壓形式為：當$i \neq j$時

$$(\mathbf{\Pi}_\alpha)_{ij} = -\eta(\frac{\partial V_j}{\partial x_i} + \frac{\partial V_i}{\partial x_j}) \tag{4.42}$$

and

$$(\mathbf{\Pi}_\alpha)_{ii} = -\eta_n \frac{\partial V_i}{\partial x_i} \tag{4.43}$$

其中阻尼係數η and η_n均是溫度的函數。 利用式(4.42)與式(4.43)可得

$$\begin{aligned}
&-(\mathbf{\Pi}_\alpha \cdot \nabla)\cdot \mathbf{V}_\alpha \\
&= -\sum_{i=1}^{3}\sum_{j=1}^{3}(\mathbf{\Pi}_\alpha)_{ij}\frac{\partial}{\partial x_j}V_i \\
&= -\sum_{i=1}^{2}\sum_{j=i+1}^{3}\{[-\eta(\frac{\partial V_j}{\partial x_i}+\frac{\partial V_i}{\partial x_j})]\frac{\partial}{\partial x_j}V_i\} - \sum_{j=1}^{2}\sum_{i=j+1}^{3}\{[-\eta(\frac{\partial V_j}{\partial x_i}+\frac{\partial V_i}{\partial x_j})]\frac{\partial}{\partial x_j}V_i\} - \sum_{i=1}^{3}[-\eta_n(\frac{\partial V_i}{\partial x_i})\frac{\partial}{\partial x_i}V_i] \\
&= -\sum_{i=1}^{2}\sum_{j=i+1}^{3}\{[-\eta(\frac{\partial V_j}{\partial x_i}+\frac{\partial V_i}{\partial x_j})]\frac{\partial}{\partial x_j}V_i\} - \sum_{i=1}^{2}\sum_{j=i+1}^{3}\{[-\eta(\frac{\partial V_i}{\partial x_j}+\frac{\partial V_j}{\partial x_i})]\frac{\partial}{\partial x_i}V_j\} - \sum_{i=1}^{3}[-\eta_n(\frac{\partial V_i}{\partial x_i})^2] \\
&= \sum_{i=1}^{2}\sum_{j=i+1}^{3}[\eta(\frac{\partial V_j}{\partial x_i}+\frac{\partial V_i}{\partial x_j})^2] + \sum_{i=1}^{3}[\eta_n(\frac{\partial V_i}{\partial x_i})^2] \geq 0
\end{aligned} \tag{4.43}$$

或

$$-(\mathbf{\Pi}_\alpha \cdot \nabla)\cdot \mathbf{V}_\alpha = \frac{1}{\eta}[(\mathbf{\Pi}_\alpha)_{xy}^2 + (\mathbf{\Pi}_\alpha)_{xz}^2 + (\mathbf{\Pi}_\alpha)_{yz}^2] + \frac{1}{\eta_n}[(\mathbf{\Pi}_\alpha)_{xx}^2 + (\mathbf{\Pi}_\alpha)_{yy}^2 + (\mathbf{\Pi}_\alpha)_{zz}^2] \geq 0 \tag{4.44}$$

將式(4.43)或式(4.44)帶入式(4.41)可得

$$\frac{3}{2}(\frac{\partial}{\partial t} + \mathbf{V}_\alpha \cdot \nabla)[\ln(p_\alpha \rho_\alpha^{-5/3})] = -\frac{(\mathbf{\Pi}_\alpha \cdot \nabla)\cdot \mathbf{V}_\alpha}{p_\alpha} \geq 0 \tag{4.45}$$

由式(4.45)與式(4.23)可知，對一個封閉的系統而言，沿著氣塊的軌跡測量此氣塊的 entropy 隨時間的變化，此氣塊的 entropy $S = (3/2)Nk_B \ln(p\rho^{-5/3})$ 絕對不會隨著時間增加而減少。這個結果與熱力學第二定律相符。

4.5.2. 由統計熱力學看熱力學第二定律

由方程式(4.37)~(4.40)可知，氣塊的熵(entropy)，可視為很多狀態$\log w = -\ln f$的統計總和。氣塊的熵(entropy)不會減少，意味著這些狀態$\log w = -\ln f$的統計總和不會減少，只能增加或持平。理論上，我們可以證明，常態分布函數的$\ln f$的統計總和，也就是

這塊氣體的焓 enthalpy $H = k_B \iiint_{Vol.} [\iiint f(\ln f) d^3v] d^3x$ 最低。因此對應的 entropy 熵值最高。由於任何分布函數，重複多次取樣的總和，都趨向常態分布函數(Snell, 1975)，所以一個系統的 entropy 熵值總是趨向最大值。因此以下三種敘述，是在講同一件事：

自然演化的結果，一個系統會趨向常態分布

自然演化的結果，一個系統會趨向最低能量（enthalpy 焓）

自然演化的結果，一個系統會趨向最大亂度（entropy 熵）

這些說法，也與熱力學第二定律的結果一致。

Exercise 4.4.

思考生命(life)的定義。探討生命(life)與熵(entropy)之間的關係。利用 google 查詢，量子物理大師薛丁格先生(Schrödinger)對生命定義的探討。

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