

0.1 Introduction

0.1.1 Review of Thermodynamics

0.1.1.1 Central Theme of Thermodynamics: Work & Heat

0.1.1.1.1 The Four Laws 0th: If two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other.

1st: The change in internal energy of a closed system is equal to the heat added to the system minus the work done by the system.

2nd: The total entropy of an isolated system can never decrease over time. In any reversible process, the total entropy of the system and its surroundings remains constant.

3rd: As the temperature approaches absolute zero, the entropy of a perfect crystal approaches a constant minimum.

$$\begin{array}{ccccc} \text{increase of internal energy} & & \text{input heat} & & \text{output work} \\ dU & = & \delta Q & - & \delta W \end{array}$$

- reversible process: $dU = TdS - PdV$
- mechanical system: $\delta W = f dx = -dV(x)$;
- *adiabatic process*(绝热过程): $\delta W = PdV = -dU$. U : thermodynamic/adiabatic potential.
- *isothermal process*(等温过程). F : isothermal potential.

$$F \equiv U - TS, \quad dF = -SdT - PdV, \quad \delta W \Big|_T = PdV = -dF$$

0.1.1.1.2 Maximum Work

- isothermal process, $A \rightarrow B$:

$$\text{1st law: } \Delta W = -\Delta U + \Delta Q$$

$$\text{2nd law: } \Delta Q \leq T(S_B - S_A)$$

$$\Delta W \leq U_A - U_B + T(S_B - S_A) = -\Delta F, \quad \Delta F = F_B - F_A$$

- $A \rightarrow B, U_A = U_B$: $\Delta W_{\max} = T(S_B - S_A)$. Example: Rubber band(橡皮筋), shrinking: $S \uparrow$.

0.1.1.1.3 Extensivity(广延) 形如 $E = E_1 + E_2$ 的广延性在传统热力学中要求短程相互作用. Assume extensive quantity X ,

$$U(\lambda S, \lambda X) = \lambda U(S, X) \xrightarrow{\partial_\lambda} \frac{\partial U(\lambda S, \lambda X)}{\partial(\lambda S)} \dot{S} + \frac{\partial U(\lambda S, \lambda X)}{\partial(\lambda X)} \dot{X} = U(S, X)$$

$$\text{let } \lambda = 1, \quad \frac{\partial U}{\partial S} \dot{S} + \frac{\partial U}{\partial X} \dot{X} = U \Rightarrow U = TS + QX, \quad Q = \frac{\partial U}{\partial X}$$

Introduce physics: $U = TS - PV + \mu N \Rightarrow dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$

$$\text{Since } dU = TdS - PdV + \mu dN$$

$$\text{So new physics: } d\mu = -sdT + vdP, \quad s = \frac{S}{N}, \quad v = \frac{V}{N}, \quad s = \left(\frac{\partial \mu}{\partial T} \right)_P, \quad v = \left(\frac{\partial \mu}{\partial P} \right)_T$$

一/二级相变分类依据: 化学势 μ 的导数连续性

一级相变. s 突变: 潜热; v 突变: 水结冰; 二级相变. $\frac{\partial s}{\partial T}$ 突变: 热容 $\left(T \frac{\partial S}{\partial T} \right)$ 变化; $\frac{\partial v}{\partial P}$ 压缩率 $\left(\frac{1}{v} \frac{\partial v}{\partial P} \right)$ 变化

0.1.1.2 Jacobian & Thermodynamics Relations

0.1.1.2.1 Definition of Jacobian (x, y) plane, functions: $\xi(x, y), \eta(x, y)$. relative functions: $x(\xi, \eta), y(\xi, \eta)$.

$$dx = \frac{\partial x}{\partial \xi} d\xi + \frac{\partial x}{\partial \eta} d\eta, \quad dy = \frac{\partial y}{\partial \xi} d\xi + \frac{\partial y}{\partial \eta} d\eta$$

$$dx \wedge dy = \frac{\partial(x, y)}{\partial(\xi, \eta)} d\xi \wedge d\eta, \quad \text{Jacobian matrix: } \frac{\partial(x, y)}{\partial(\xi, \eta)} = \begin{vmatrix} \frac{\partial x}{\partial \xi} & \frac{\partial x}{\partial \eta} \\ \frac{\partial y}{\partial \xi} & \frac{\partial y}{\partial \eta} \end{vmatrix} = \begin{vmatrix} J_{11} & J_{12} \\ J_{21} & J_{22} \end{vmatrix}$$

正则变换: $J = 1$, 相空间体积不变. State function \leftrightarrow total differential(全微分) $\leftrightarrow J = 1$:

$$dU = TdS - PdV = \frac{\partial U}{\partial x} dx + \frac{\partial U}{\partial y} dy \Rightarrow T = \left(\frac{\partial U}{\partial S} \right)_V, -P = \left(\frac{\partial U}{\partial V} \right)_S$$

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}, \quad \text{derivative exchange symmetry}$$

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \Rightarrow \frac{\partial(T, S)}{\partial(P, V)} = 1, \quad \text{Maxwell's relation(s)}$$

$$dT \wedge dS = \frac{\partial(T, S)}{\partial(P, V)} dP \wedge dV, \quad J = 1 \text{ 和温标选取对应}$$

0.1.1.2.2 Property of Jacobian Matrix

1. $\frac{\partial(T, S)}{\partial(P, V)} = \frac{\partial(T, S)}{\partial(\mu, \nu)} \frac{\partial(\mu, \nu)}{\partial(P, V)} = 1$, to produce numerous Maxwell's relations;

[Example] let $(\mu, \nu) = (V, S)$, $\frac{\partial(T, S)}{\partial(V, S)} \frac{\partial(V, S)}{\partial(P, V)} = 1 \Rightarrow \left(\frac{\partial T}{\partial V} \right)_S \cdot \left(-\frac{\partial S}{\partial P} \right)_V = 1 \Rightarrow \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$

As $\left(\frac{\partial \gamma}{\partial \mu} \right)_\nu$, variables γ, μ, ν as P, V, T, S . $\frac{1}{2} A_4^3 = 12$. Write down these elements as a big matrix:

$$\begin{bmatrix} \left(\frac{\partial V}{\partial P} \right)_T & \left(\frac{\partial P}{\partial T} \right)_V & \left(\frac{\partial V}{\partial P} \right)_T \\ \vdots & \vdots & \vdots \end{bmatrix}_{4 \times 3}, \quad \text{Only 3 elements are independent.}$$

$$2. \frac{\partial(x, y)}{\partial(\xi, y)} = \left(\frac{\partial x}{\partial \xi} \right)_y; 3. \frac{\partial(y, x)}{\partial(\xi, \eta)} = - \frac{\partial(x, y)}{\partial(\xi, \eta)}$$

0.1.1.3 Exterior derivative(外微分)

p -form $\xrightarrow{d} p + 1$ -form. 0-form: $f(x) \rightarrow df(x) = \frac{df(x)}{dx} dx$;

1-form: $g(x, y)dx \rightarrow d[g(x, y)dx] = \left(\frac{\partial g}{\partial x} dx + \frac{\partial g}{\partial y} dy \right) \wedge dx = \frac{\partial g}{\partial y} dy \wedge dx, \quad dx \wedge dy = -dy \wedge dx \Rightarrow d^2 = 0$;

2-form: $f(x, y)dx \wedge dy$

$$dU = TdS - PdV \Rightarrow d(dU) = d(TdS) - d(PdV) \Rightarrow 0 = dT \wedge dS - dP \wedge dV \Rightarrow dT \wedge dS = dP \wedge dV$$

$$d^2 = 0 \Rightarrow dT \wedge \left[\left(\frac{\partial S}{\partial V} \right)_T dV + \cancel{\left(\frac{\partial S}{\partial T} \right)_V dT} \right] = \left[\cancel{\left(\frac{\partial P}{\partial V} \right)_T dV} + \left(\frac{\partial P}{\partial T} \right)_V dT \right] \wedge dV \Rightarrow \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

0.1.2 Some Key Concepts in Thermodynamics

0.1.2.1 Temperature

0.1.2.1.1 Thermodynamic Perspective $dU = TdS - PdV$, $T \equiv \left(\frac{\partial U}{\partial S} \right)_V$, thermodynamic definition of temperature.

1st law: $E = E_1 + E_2 = \text{const.}$

$$\frac{dS}{dE_1} = 0, \quad \text{condition of thermal equilibrium}$$

$$\frac{dS_1}{dE_1} + \frac{dS_2}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{dE_2}{dE_1} = \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2} = 0 \Rightarrow \frac{dS_1}{dE_1} = \frac{dS_2}{dE_2} \Leftrightarrow \frac{1}{T_1} = \frac{1}{T_2}$$

$$\text{2nd law: } \frac{dS}{dt} \geq 0 \Rightarrow \frac{dS}{dE_1} \frac{dE_1}{dt} \geq 0 \Rightarrow \left(\frac{dS_1}{dE_1} - \frac{dS_2}{dE_2} \right) \frac{dE_1}{dt} \geq 0 \Rightarrow \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt} \geq 0$$

$$\text{if } T_2 > T_1, \quad \frac{1}{T_1} - \frac{1}{T_2} > 0 \Rightarrow \frac{dE_1}{dt} \geq 0$$

*Gibbs' geometric viewpoint of thermodynamics $U(S, V)$.

0.1.2.1.2 Kinetic Viewpoint Microscopic structure of the system needed. Ideal gas, Maxwell distribution(3D):

$$P(\vec{v})d^3\vec{v} = A \exp \left[-\frac{mv^2/2}{k_B T} \right] d^3\vec{v}$$

$$\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle) = \frac{3}{2}k_B T, \quad \langle v_x^2 \rangle = \int v_x^2 P(\vec{v})d^3\vec{v}$$

[Example] Rod particles in thermal equilibrium. 若棒的长轴为 z 轴, 则角动量 \vec{J} 倾向于 平行/垂直 于 z 轴. 每个自由度都是分得 $\frac{1}{2}k_B T$ 的能量.

$$\frac{1}{2}I_z \overline{\omega_z^2} = \frac{1}{2}k_B T, \quad \frac{1}{2}I_x \overline{\omega_x^2} = \frac{1}{2}k_B T$$

$$I_z \ll I_x = I_y \Rightarrow \overline{\omega_z^2} \gg \overline{\omega_x^2} = \overline{\omega_y^2}$$

$$\frac{J_z}{J_x} = \frac{I_z \omega_z}{I_x \omega_x} \approx \frac{\omega_z}{\omega_x} \ll 1 \Rightarrow J_z \ll J_x \Rightarrow \vec{J} \text{ 主要在 } x-y \text{ 平面}$$

0.1.2.2 Entropy

0.1.2.2.1 Thermodynamic Perspective For a reversible cyclic process, $\oint \frac{\delta Q}{T} = 0$. δQ : heat absorbed by the system.

$$\forall \text{ reversible process, } \int_{\Gamma_{A \rightarrow B}} \frac{\delta Q}{T} + \int_{\Gamma_{B \rightarrow A}} \frac{\delta Q}{T} = 0 \Rightarrow \int_{\Gamma_{A \rightarrow B}} \frac{\delta Q}{T} \text{ is independent of the path.}$$

State variable $dS \equiv \frac{\delta Q}{T}$ reflects intrinsic property of the system. 熔化热(相变潜热), 吸热而 T 不变(change of state).

$$\text{2nd law: } \oint \frac{\delta Q}{T} \leq 0, \quad \forall \text{ process}$$

$$\int_{\gamma_{A \rightarrow B}^{(I)}} \frac{\delta Q}{T} + \int_{\gamma_{B \rightarrow A}^{(R)}} \frac{\delta Q}{T} \leq 0, \quad \text{(I) for Irreversible, (R) for reversible}$$

$$\Rightarrow S(B) - S(A) \geq \int_{\Gamma_{A \rightarrow B}^{(I)}} \frac{\delta Q}{T} \Rightarrow \text{isolated system: } S(B) - S(A) \geq 0$$

0.1.2.2.2 Boltzmann's Entropy Statistical interpretation of thermodynamics. $S = k \ln W$,

1. closed/isolated system. W : number of microstates. states: $(q, p); (0, 1); |n\rangle$, distinguishable(等价, 不可区分).

2. 两系统微观态数 W_1, W_2 . 熵广延性 $S = S_1 + S_2 = k \ln W_1 + k \ln W_2 = k \ln (W_1 W_2)$. \ln : 化 \times 为 $+$.

3. $W = e^{S/k} \sim e^{O(N)}$, W : thermodynamic probability.

[Example] Closed system consisted of N non-interacting oscillators. 各振子 k 处于 $|k\rangle$ 状态. 总能量为 E . distribution of energy? n_k 为处于 $|k\rangle$ 状态的振子数目且充分大.

$$\sum_k \varepsilon_k n_k = E = \text{const.}, \quad \sum_k n_k = N$$

$$\exists \{n_k\} \text{ s.t. } W = \frac{N!}{\prod_k n_k!} \text{ reaches max } \xrightarrow{\ln M! = M \ln M - M} \ln W = - \sum_k n_k \ln \frac{n_k}{N}, \quad (\# \ln \#)$$

拉格朗日乘法: $I = \ln W - \alpha \sum_k n_k - \beta \sum_k n_k \varepsilon_k, \quad \delta n_k \rightarrow \delta I = 0 \Rightarrow n_k^* = \frac{e^{-\beta \varepsilon_k}}{\sum_k e^{-\beta \varepsilon_k}}, \quad \text{Boltzmann factor}$

Stirling's formula: $\ln N! = N \ln N - N$

$$N! = \Gamma(N+1) = \int_0^\infty e^{-x} x^N dx = \int_0^\infty e^{-S(x)} dx$$

$$S(x) \approx S(x_0) + \frac{1}{2} \frac{\partial^2 S(x)}{\partial x^2} \Big|_{x_0} (x - x_0)^2 + \dots, \quad \frac{\partial S_x}{\partial x} \Big|_{x_0} = 0$$

$$\Rightarrow N! \simeq N^N e^{-N} (2\pi N)^{\frac{1}{2}}$$

0.1.2.2.3 Gibbs' Entropy Open system: $S = -k_B \sum_i P_i \ln P_i$. 微观态处于 $|i\rangle$ 的概率为 P_i .

1. 使得 S 最大的 $\{P_i\}$ 为等概率分布. [Example] 两状态系统.

2. $P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{e^{-\beta E_i}}{Z}, \quad S = \frac{\langle E \rangle}{T} + k_B \ln Z, \quad -k_B T \ln Z = \langle E \rangle - TS.$

0.1.3 Learn Thermodynamics by Examples/Applications

0.1.3.1 Ideal Gas

0.1.3.1.1 Entropy

$$dU = TdS - PdV \Leftrightarrow TdS = dU + PdV$$

If $V = \text{const.}$: $dU = TdS \Rightarrow \frac{\partial S(U, V)}{\partial U} \Big|_V = T(U, V)$

$$S(U, V) - S(U_0, V) = \int_{U_0}^U \frac{1}{T(U, V)} dU, \quad \text{ideal gas: } U = \frac{3}{2} k_B T N$$

$$\Rightarrow S(U, V) - S(U_0, V) = \frac{3}{2} N k_B \ln \left(\frac{U}{U_0} \right);$$

$$\text{similarly, } S(T, V) - S(T_0, V) = \frac{3}{2} N k_B \ln \left(\frac{T}{T_0} \right)$$

[Discussion] 1. Extensivity: $S \propto N$; Dimension(量纲); 2. Physics: log-dependence on U and T @ high T (low response)

0.1.3.2 Electromagnetic Radiation @ Thermodynamic Viewpoint

Stafan-Boltzmann Law: $U = bVT^4, \quad b = 7.65 \times 10^{-16} \text{ J/m}^3 \text{ K}^4$

$$dU = TdS - PdV \xrightarrow{\frac{dV}{dV}} \frac{\partial U(T, V)}{\partial V} = T \frac{\partial S(T, V)}{\partial V} - P \quad \frac{\partial S(T, V)}{\partial V} = \frac{\partial P(T, V)}{\partial T} \quad bT^4 = T \frac{\partial P(T, V)}{\partial T} - P \Rightarrow P = \frac{b}{3} T^4$$

$$U = TS - PV \quad (\text{for extensive system}) \Rightarrow P = \frac{1}{3} \frac{U}{V}, \quad S = \frac{4}{3} b^{\frac{1}{4}} U^{\frac{3}{4}} V^{\frac{1}{4}} \sim T^3$$

对光子而言, "化学势" 为 0. 所以很容易因为升温激发出光子.

[Example] 更多高响应体系的例子: 1. Bending rigidity: $B \sim h^3$; 2. Power in fusion: $\sim B^4$;

0.1.3.3 Rubber Band

前置: 1. thermodynamic laws(general); 2. equation of state, molecular/microscopic model

0.1.3.3.1 定性分析 假定为快速拉伸, 即设 $\Delta Q = 0$. 拉长后构型减少, 即其构型熵 S_{conf} 减少, $T\Delta S_{\text{conf}} \downarrow$; 长链分子本身也在振动, 振动熵 S_{vib} 上升使得总热量为 0. 因此温度 $T \uparrow$. 相应地, 一个绷直的橡皮筋快速收缩会 $T \downarrow$.

假定橡皮筋垂吊一重物 G . 可将其视为一(低效)热机. 收缩之后, 其构型熵增加. 所以若要使得其收缩/做功, 令其吸热即可.

0.1.3.3.2 定量分析 L : 长度; τ : tension(张力); T : 温度, U : 内能.

$L_0 < L < L_1$, U 对 L 无关; τ 随着 T 升高而增大.

$$U = cL_0T, \quad U \sim T$$

$$\tau = bT \frac{L - L_0}{L_1 - L_0}, \quad \text{self-consistent condition: } \frac{\partial^2 S}{\partial U \partial V} = \frac{\partial^2 S}{\partial V \partial U}$$

$$\Rightarrow dS = \frac{1}{T}dU - \frac{\tau}{T}dL = cL_0 \frac{dU}{U} - b \frac{L - L_0}{L_1 - L_0} dL \xrightarrow{f} S = S_0 + cL_0 \ln \frac{U}{U_0} - b \frac{(L - L_0)^2}{2(L_1 - L_0)}, \quad \text{entropy elasticity}$$