- 过程的方向性.

(1) 第二定律: U,V 固定. $\Delta S \geq 0$.

(2) T,V 固定

$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S$$

T,V fixed, $Q \leq T\Delta S \Rightarrow \Delta F \leq 0$.

注: 指的是初态和末态! (?) 这是因为 $\int đQ = \int T dS$ 中,

$Q \leq T\Delta S$ 是一个跳跃的等式!! T始终是环境温度! 只要环境温度不变即可.

(3) T,p 固定

$$\Delta G = \Delta U - T\Delta S + p\Delta V = Q - T\Delta S \leq 0.$$

⊙ 关键是要明白: 在有限温的系统中, U 最小不是最优的.

例如, $F = U - TS$. 有 "Energy" 和 "Entropic" term.

后者反映宏观热力学过程的不可逆性/大量粒子的统计性质

因此通常情况下, S 要变大, $F = U - TS$ 同时受二者支配, 不是简单的 U_{min}/S_{max}.

这是合理的, 因为 U_{min} 对应全部粒子到基态. 这与大量粒子的统计是相违背的.

- 麦克斯韦关系. (固定N)

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

交换偏导数: $\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$

$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$. 剩下的以此类推.

- 用处: 把不好观测的量转变为好观测的量.
- 例: 热容

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

理想气体: $C_p - C_V = Nk_B$. 一般情况如何?

$$S = S(T,p) = S(T, V(T,p))$$

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p - C_V = T \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\text{不好测}} \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{\text{可以测}}$$

代换: $\left(\frac{\partial S}{\partial V}\right)_T$, 找 V,T 函数

$\Rightarrow F = F(V,T) \quad dF = -SdT - pdV$.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V.$$

$$C_p - C_V = T \cdot \underbrace{\left(\frac{\partial p}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_p}_{\text{响应函数 Response function}}$$

- 膨胀率 Expansivity $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$
- 压缩系数 Compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$.

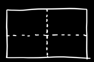
利用 $\left(\frac{\partial p}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_p \cdot \left(\frac{\partial V}{\partial p}\right)_T = -1$.

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial V}{\partial T}\right)_p \Big/ \left(-\frac{\partial V}{\partial p}\right)_T = \frac{V\alpha}{V\kappa_T} = \frac{\alpha}{\kappa_T}.$$

代入，即有

$$C_p - C_V = \frac{VT\alpha^2}{\kappa_T} \geq 0.$$

• 相平衡条件



把体系分割成均匀的子系统.

$$S = S(U,V,N) = \sum_a S^a(U^a,V^a,N^a)$$

现在要做的：寻找 U^a, V^a, N^a，使熵 S 最大.

孤立体系约束条件：

$$\sum U^a = U, \quad \sum V^a = V, \quad \sum N^a = N.$$

条件极值 → 拉格朗日乘子.

$$f(U,V,N) = \sum S^a(U^a,V^a,N^a) - \alpha\sum_a U^a - \beta\sum_a V^a - \gamma\sum_a N^a.$$

f 最大：

$$\begin{cases} \frac{\partial f}{\partial U^a} = 0 \Rightarrow \frac{\partial S^a}{\partial U^a} = \alpha \Rightarrow \frac{1}{T^a} = \alpha, \ \forall a \\ \frac{\partial f}{\partial V^a} = 0 \Rightarrow \frac{\partial S^a}{\partial V^a} = \beta \Rightarrow \frac{p^a}{T^a} = \beta, \ \forall a \\ \frac{\partial f}{\partial N^a} = 0 \Rightarrow \frac{\partial S^a}{\partial N^a} = \gamma \Rightarrow -\frac{\mu^a}{T^a} = \gamma, \ \forall a \end{cases}$$

$[dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN]$

因此，在平衡态时：

$$\begin{cases} T_1 = T_2 = \cdots = T. & \text{"thermal"} \\ p_1 = p_2 = \cdots = p. & \text{"mechanical"} \\ \mu_1 = \mu_2 = \cdots = \mu. & \text{"chemical"} \end{cases}$$

向平衡态的演化？

$\boxed{T_1 \mid T_2}$ $\quad T_1 > T_2$

$$S = S_1(U_1,V_1,N_1) + S_2(\underbrace{U_2}_{U-U_1},V_2,N_2)$$

$$\delta S = \frac{\partial S_1}{\partial U_1}\delta U_1 + \frac{\partial S_2}{\partial U_2}(-\delta U_1) = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta U_1 > 0.$$

$\frac{1}{T_1} < \frac{1}{T_2}$, $\delta U_1 < 0$. ⇒ 热量从高温流向低温.

同理，$\mu_1 > \mu_2 \Rightarrow \delta S = \left(-\frac{\mu_1}{T} + \frac{\mu_2}{T}\right)\delta N_1 > 0.$

⇒ 粒子数从高化学势流向低化学势.

• 平衡的稳定条件 [确定S是极大]

$$\sum_a \frac{\partial^2 S^a}{\partial x_i \partial x_j}\delta x_i \delta x_j \leq 0. \quad \{x_i\} = \{U^a, V^a, N^a\}.$$

↓

Hessian Matrix : negative semi-definite 半负定.

$$\frac{\partial}{\partial x_j}\left(\underbrace{\frac{\partial S^a}{\partial x_i}}_{\text{"Force" } J_i\text{，与 } x_i \text{ 共轭}}\right)\delta x_i \delta x_j$$

$$\frac{\partial J_i}{\partial x_j}\delta x_j = \delta J_i$$

$\Rightarrow \delta J_i \delta x_i \leq 0.$ 对偶的！ $\quad [dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN]$

即 $\delta\left(\frac{1}{T}\right)\delta U + \delta\left(\frac{p}{T}\right)\delta V - \delta\left(\frac{\mu}{T}\right)\delta N \leq 0.$ [这里 $\delta^2 S$ 不考虑 Lagrange 乘子，因为那些都是一阶的，求二阶导之后都没有了]

$$-\frac{\delta T}{T^2}\delta U+\frac{T\delta p-p\delta T}{T^2}\delta V-\frac{T\delta\mu-\mu\delta T}{T^2}\delta N\le 0.$$

提取δT项：

$$-\frac{\delta T}{T^2}\underbrace{(\delta U+p\delta V-\mu\delta N)}_{T\delta S}+\frac{\delta p\delta V-\delta\mu\delta N}{T}\le 0.$$

$\Rightarrow$ $\delta T\delta S-\delta p\delta V+\delta\mu\delta N\ge 0$. for $\forall a$. 子系统的稳定条件

另一种解释：关子是线性的，二阶变动下可以认为是独立的

(这个待查/证. 今天没状态. 先不证了)

这里确实是$\forall a$. 林宗涵书上有解释.

[理解：选取三个独立变量做虚变动，得到另外三个. 代进去≥ 0]

$$\delta T\delta S-\delta p\delta V+\delta\mu\delta N$$
$$=\delta T\delta S-\delta p\delta V+\delta N\cdot(-s\delta T+v\delta p)$$
$$=N(\delta T\delta s-\delta p\delta v).$$

$$\sum_a \underset{\downarrow\ \text{广延量}}{N^a}(\delta T^a\delta s^a-\underset{\downarrow\ \text{强度量}}{\delta p^a}\delta v^a)\ge 0$$

对给定的a：把其他$N^{a'}$取成0，得到

$$\delta T^a\delta s^a-\delta p^a\delta v^a\ge 0,\quad\forall a$$

还原：

$$\delta T^a\delta S^a-\delta p^a\delta V^a+\delta\mu^a\delta N^a\ge 0,\quad\forall a.$$

现在考虑 $\delta N=0$: N fixed

$$\delta T\delta S-\delta p\delta V\ge 0.$$

$S=S(T,V)$　$p=p(T,V)$

$$\delta T\left[\left(\frac{\partial S}{\partial T}\right)_V\delta T+\left(\frac{\partial S}{\partial V}\right)_T\delta V\right]-\delta V\left[\left(\frac{\partial p}{\partial T}\right)_V\delta T+\left(\frac{\partial p}{\partial V}\right)_T\delta V\right]\ge 0.$$

交叉项和$=0$

$$\Rightarrow\left(\frac{\partial S}{\partial T}\right)_V(\delta T)^2-\left(\frac{\partial p}{\partial V}\right)_T(\delta V)^2\ge 0.$$

$$\frac{C_V}{T}(\delta T)^2+\frac{1}{V\kappa_T}(\delta V)^2\ge 0.$$

稳定性要求：$C_V>0$, $\kappa_T>0$.

$f(x_i)$

$\frac{\partial f}{\partial x_i}\delta x_i=0.\Rightarrow\frac{\partial f}{\partial x_i}=0,\ \forall i.$

$\frac{\partial^2 f}{\partial x_i\partial x_j}\delta x_i\delta x_j\le 0.$

$\sum\lambda_i x_i=0.$

$\frac{\partial f}{\partial x_i}\delta x_i+\mu(\sum\lambda_i\delta x_i)=0.$　这个操作..?

$\Rightarrow\frac{\partial f}{\partial x_i}=-\mu\lambda_i.$

$\delta f=0.$

$\frac{\partial f}{\partial x_i}\delta x_i=0.$

$F(x_1\cdots x_n)=0.$

$f(x_i)-\lambda\cdot F(x_i)$　$\lambda\cdot\sum\frac{\partial F}{\partial x_i}\delta x_i=0$

$\left(\frac{\partial f}{\partial x_i}-\lambda\frac{\partial F}{\partial x_i}\right)\delta x_i=0.$

$-F(x_i)\delta\lambda=0$

$f(x_1,\cdots,x_{n-1},x_n(\cdots))$

$\frac{\partial f}{\partial x_i}+\frac{\partial f}{\partial x_n}\cdot\frac{\partial x_n}{\partial x_i}=0.$

$\varphi(x_1\cdots x_n)=0$

$\frac{\partial\varphi}{\partial x_i}dx_i=0$

$\frac{\partial x_n}{\partial x_i}=-\frac{\frac{\partial\varphi}{\partial x_i}}{\frac{\partial\varphi}{\partial x_n}}$

$\frac{\partial f}{\partial x_i}\frac{\partial\varphi}{\partial x_n}=\frac{\partial f}{\partial x_n}\frac{\partial\varphi}{\partial x_i}$

$$\frac{\partial f}{\partial x_i}-\frac{\frac{\partial f}{\partial x_n}}{\frac{\partial\varphi}{\partial x_n}}\frac{\partial\varphi}{\partial x_i}=0.$$

λ

$$\begin{cases}\frac{\partial f}{\partial x_i}-\lambda\frac{\partial\varphi}{\partial x_i}=0\\ \frac{\partial f}{\partial x_n}-\lambda\frac{\partial\varphi}{\partial x_n}=0\end{cases}$$

$\Rightarrow$ f 二阶变动？　　Σx_j

$\frac{\partial^2 f}{\partial x_i\partial x_j}$　$\frac{\partial}{\partial x_n}\frac{\partial f}{\partial x_i}$

$\frac{\partial}{\partial x_i}(\ )\cdot\frac{\partial x_n}{\partial x_i}$

$\frac{\partial}{\partial x_i}=\frac{\partial f}{\partial x_i}+\frac{\partial f}{\partial x_n}\frac{\partial x_n}{\partial x_i}$　$\frac{\partial}{\partial x_j}\left(\frac{\partial f}{\partial x_n}\frac{\partial x_n}{\partial x_i}\right)$

$\frac{\partial}{\partial x_j}(\ )=\frac{\partial^2 f_i}{\partial x_i\partial x_j}+\frac{\partial}{\partial x_n}\left(\frac{\partial f}{\partial x_i}\right)\cdot\frac{\partial x_n}{\partial x_j}+\frac{\partial}{\partial x_j}\left(\frac{\partial f}{\partial x_n}\right)\frac{\partial x_n}{\partial x_i}$ ✓

$\frac{\partial^2 f_i}{\partial x_i\partial x_j}$ $(n-1,n-1)$　$\frac{\partial^2 f}{\partial x_n\partial x_i}$　$1\sim n-1$

$+\frac{\partial}{\partial x_n}\left(\frac{\partial f}{\partial x_n}\right)\frac{\partial x_n}{\partial x_i}\frac{\partial x_n}{\partial x_j}$

λ是要解出来的. ✓

$\lambda=\frac{\frac{\partial f}{\partial x_n}}{\frac{\partial\varphi}{\partial x_n}}$　(这是因为$\varphi(\ )=0$)