第二章：均匀物质的热力学性质

[数学准备]

1、隐函数偏微分

函数$z=z(x,y)$ 满足 $F(x,y,z)=0$

$$\left(\frac{\partial z}{\partial x}\right)_y = 1\Big/\left(\frac{\partial x}{\partial z}\right)_y$$

$$\left(\frac{\partial z}{\partial y}\right)_x = 1\Big/\left(\frac{\partial y}{\partial z}\right)_x$$

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1.$$

2、 二元函数的全微分(式)

若： $z = z(x, y)$

则： $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

为函数 z 的“全微分”

则必有： $$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$$

即： $$\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)$$

也即：偏微分运算的先后顺序可以交换！！

3、雅可比行列式

设u,v是独立变数x,y的函数 $u = u(x, y), v = v(x, y)$

雅可比定义为: $$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x}, & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x}, & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x}.$$

性质

(1) $$\left(\frac{\partial u}{\partial x}\right)_y = \frac{\partial(u,y)}{\partial(x,y)}$$

(2) $$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)}$$

(3) $$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(x,s)}\frac{\partial(x,s)}{\partial(x,y)}$$

§2-1　热力学函数的全微分

主要目的：

利用数学方法 ⟶ 热力学函数间微分关系

已有的知识：

- 基本的热力学函数
- 内能U、自由能F、焓H、吉布斯(Gibbs)函数G

$$H=U+PV,\qquad F=U-TS,\qquad G=H-TS$$

物态方程、内能和熵

讨论对象：**简单系统**的无摩擦准静态过程，

即“可逆过程”

状态函数和自变量的选取

自变量：

S，p，V，T

状态函数：

U，H，F，G

状态函数和自变量按如下组合：

$$U = U(S, V), \quad H = H(S, p)$$

$$F = F(T, V), \quad G = G(T, p)$$

热力学的基本微分方程(只考虑体积变化功)

$$dU=TdS-pdV$$

(1) 内能：$U=(S,V)$，全微分为

$$dU=\left(\frac{\partial U}{\partial S}\right)_V dS+\left(\frac{\partial U}{\partial V}\right)_S dV$$

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

偏导数的次序可以交换

$$\frac{\partial^2 U}{\partial S\partial V}=\frac{\partial^2 U}{\partial V\partial S}$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial p}{\partial S}\right)_V} \qquad (1)$$

(2) 焓的定义 $H=U+PV$

$dU=TdS-pdV \Rightarrow dH=TdS+Vdp$

$$\left(\frac{\partial H}{\partial S}\right)_P=T,\left(\frac{\partial H}{\partial p}\right)_S=V$$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_S=\left(\frac{\partial V}{\partial S}\right)_P} \qquad (2)$$

(3) 自由能 $F=U-TS$

$$dF=-SdT-pdV$$

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

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V} \qquad (3)$$

(4) 吉布斯(Gibbs)函数 $G=U+pV-TS$

$$dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial P}\right)_P = -S, \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P} \qquad (4)$$

(1—4) 麦克斯韦(Maxwell)关系，or 麦氏关系

[麦克斯韦关系的总结]

1. 热力学基本方程　　　　2. 全微分

$$dU = TdS - pdV \xrightarrow{U=U(S,V)} dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$dH = TdS + Vdp \xrightarrow{H=H(S,p)} dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

$$dF = -SdT - pdV \xrightarrow{F=F(T,V)} dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

$$dG = -SdT + Vdp \xrightarrow{G=G(T,p)} dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

3. S，p，V，T 与U，H，F，G一阶偏导数的关系

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

$$T=\left(\frac{\partial H}{\partial S}\right)_p \quad , \quad V=\left(\frac{\partial H}{\partial p}\right)_S$$

$$S=-\left(\frac{\partial F}{\partial T}\right)_V \quad , \quad p=-\left(\frac{\partial F}{\partial V}\right)_T$$

$$S=-\left(\frac{\partial G}{\partial T}\right)_p \quad , \quad V=\left(\frac{\partial G}{\partial p}\right)_T$$

4.麦克斯韦偏微分关系

是“S，p，V，T一阶偏导数之间的关系”

也是“U，H，F，G二阶偏导数之间的关系”

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad \text{(麦01)} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad \text{(麦03)}$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p \quad \text{(麦02)} \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad \text{(麦04)}$$

同样，可从联络图中找出

全部“麦克斯韦关系”！！