Legendre变换下的函数与自变量转换

热力学基本方程

$dU = TdS - pdV$

$H = U + pV$

$dH = TdS + Vdp$

$F = U - TS$

$dF = -SdT - pdV$

$G = U - TS + pV$

$dG = -SdT + Vdp$

Maxwell关系

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

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

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

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

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

物理上 $dU = TdS - pdV$

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

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

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

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

记忆: $dU = TdS - pdV \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$

Maxwell关系的简单应用

1. 导出以可测量量表示的 $\left(\frac{\partial U}{\partial V}\right)_T$

$dU = TdS - pdV$

$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$$dU = \underbrace{T\left(\frac{\partial S}{\partial T}\right)_V}_{\text{据定义}} dT + \underbrace{\left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right]}_{\text{Maxwell}} dV$$

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

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

2. 导出以可测量量表示的 $\left(\frac{\partial H}{\partial p}\right)_T$

$dH = TdS + Vdp$

$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$

$$dH = \underbrace{T\left(\frac{\partial S}{\partial T}\right)_p}_{\text{据定义}} dT + \underbrace{\left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]}_{} dp$$

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

$-T\left(\frac{\partial V}{\partial T}\right)_p + V = \left(\frac{\partial H}{\partial p}\right)_T$

$C_p - C_V = T\left(\frac{\partial S}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_V$

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

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

$$C_p - C_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \overset{\text{Maxwell}}{=\!=} T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = \frac{VT\alpha^2}{\kappa_T}$$

e.g. 理想气体 $C_p - C_V = nR$

体胀系数 $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

压强系数 $\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$

等温压缩系数 $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

热力学函数

基本：物态方程 内能 熵 ⟶ 其它函数

1. 已知 C_V 和物态方程 $p=p(T,V)$ ⟶ 内能、熵

$dU = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV$

$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$\quad = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV$

2. 已知 C_p 和物态方程 $V=V(T,p)$ ⟶ 焓、熵

$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$

$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$

$\quad = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_p dp$

特性函数

选自然变量，只要知道一个热力学函数，就可完全确定均匀系统平衡性质.

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

热辐射的热力学理论

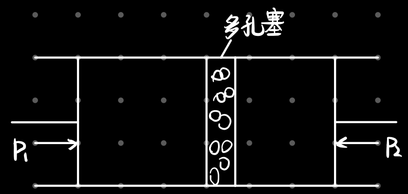
$U(T,V) = u(T)V \quad \left(\frac{\partial U}{\partial V}\right)_T = u(T) \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \quad p = \frac{1}{3}u$

$u = \frac{T}{3}\frac{du}{dT} - \frac{u}{3} \Rightarrow u = aT^4 \quad dS = \frac{dU + pdV}{T} \Rightarrow S = \frac{4}{3}aT^3V$

$G = U - TS + pV \Rightarrow G = 0$ 平衡辐射光子数不守恒的结果

获得低温的方法 $\begin{cases} \text{气体的节流过程} \\ \text{气体的绝热膨胀过程} \\ \text{顺磁性固体的磁冷却法} \end{cases}$

1. 气体的节流过程 ※绝热



$H = H(T, p)$

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = -\frac{V - T\left(\frac{\partial V}{\partial T}\right)_p}{C_p}$$

$U_2 - U_1 = P_1V_1 - P_2V_2$

$U_2 + P_2V_2 = U_1 + P_1V_1 \quad H_1 = H_2$

定义 $\mu = \left(\frac{\partial T}{\partial p}\right)_H$ 焦耳-汤姆孙系数

$$\mu = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] = \frac{V}{C_p}(T\alpha - 1)$$

对理想气体，$\alpha = \frac{1}{T}$，$\mu = 0$ 节流前后温度不变

对实际气体，若 $\alpha T > 1$，有 $\mu > 0$；若 $\alpha T < 1$，有 $\mu < 0$

2. 气体的绝热膨胀过程 ※准静态

准静态绝热过程中 $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp = 0$

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p = \frac{VT\alpha}{C_p} > 0$$

膨胀，温度必然下降

3. 顺磁性固体的磁冷却法

忽略体积变化 $dU = TdS + \mu_0 H\, dm$ 即可通过代换 $p \to -\mu_0 H,\ V \to m$

由 $\left(\frac{\partial T}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p \Rightarrow \left(\frac{\partial T}{\partial H}\right)_S = -\frac{\mu_0 T}{C_H}\left(\frac{\partial m}{\partial T}\right)_m$

顺磁介质遵从居里定律 $m = \frac{CV}{T}H \Rightarrow \left(\frac{\partial T}{\partial H}\right)_S = \frac{CV}{C_H T}\mu_0 H$