热力学统计物理第四次作业

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1

由定义可知:

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

则有:

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

利用热力学基本方程与麦克斯韦关系可知:

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

则有:

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \left(\frac{\partial}{\partial T}\left(-T\left(\frac{\partial V}{\partial T}\right)_p + V\right)\right)_p = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

考虑 $(\partial C_V/\partial V)$:
有定义可知:

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

则有:

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

利用热力学基本方程与麦克斯韦关系可知:

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

则有:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right)\right)_V = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

利用热力学基本关系可知:

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

令 $S(T,p)=S(T,V(T,p))$，则有:

$$\begin{aligned}
dS&=\left(\frac{\partial S}{\partial T}\right)_p dT+\left(\frac{\partial S}{\partial p}\right)_T dp\\
&=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T dV\\
&=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p dT+\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T dp
\end{aligned}$$

则有:

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

利用麦克斯韦关系可得:

$$\begin{aligned}
C_p-C_V&=T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\\
&=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p\\
&=\frac{T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p\left(-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial V}{\partial T}\right)_p\right)}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}\\
&=\frac{TV\left(\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right)^2}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}
\end{aligned}$$

其中有:

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial V}{\partial p}\right)_T=-1,\ \kappa_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T,\ \beta_p=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

则有:

$$C_p-C_V=\frac{TV\beta_p^2}{\kappa_T}$$

3

由 Jacobi 行列式性质可知:

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

则有:

$$\frac{\kappa_T}{\kappa_S} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}{\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\frac{\partial(V,T)}{\partial(p,T)}}{\frac{\partial(V,S)}{\partial(p,S)}} = \frac{\frac{\partial(p,S)}{\partial(p,T)}}{\frac{\partial(V,S)}{\partial(V,T)}} = \frac{T\left(\frac{\partial S}{\partial T}\right)_p}{T\left(\frac{\partial S}{\partial T}\right)_V} = \frac{C_p}{C_V} = \gamma$$

其中利用了由热力学基本微分方程推得的:

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

4

由于物质的温度保持不变，则其内能不发生变化，由热力学第一定律可知，磁化过程中释放出的热量为:

$$Q = -\Delta U + W = \int_0^H \mu_0 V H\, dM = \int_0^H \frac{\mu_0 C V H}{T}\, dH = \frac{\mu_0 C V H^2}{2T}$$

即磁化过程中释放出的热量为: $\frac{\mu_0 C V H^2}{2T}$

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5.1

对 $S = S(T,V)$ 做全微分得:

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

由热力学基本微分方程可知:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V}{T}$$

利用麦克斯韦关系与范德瓦尔斯气体状态方程可知:

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

则有:

$$\begin{aligned}
S(T,V) &= \int dS = \int_{T_0}^{T} \frac{C_V}{T}\, dT + \int \frac{\nu R}{V - nb}\, dV + S_0 \\
&= \int_{T_0}^{T} \frac{C_V}{T}\, dT + \nu R \ln(V - \nu b) + S_0
\end{aligned}$$

5.2

设 $U = U(T,V)$，则有:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

由热力学基本方程以及麦克斯韦关系可知:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{\nu RT}{V - \nu b} - \frac{\nu RT}{V - \nu b} + \frac{a\nu^2}{V^2} = \frac{a\nu^2}{V^2}$$

则有:

$$dU = C_V\, dT + \frac{a\nu^2}{V^2}\, dV$$

两侧积分可得:

$$U = U_0 + \int_{T_0}^{T} C_V\, dT' - \frac{a\nu^2}{V}$$

则自由能为:

$$\begin{aligned}
F(T,V) &= U - TS = U_0 + \int_{T_0}^{T} C_V\, dT' - \frac{a\nu^2}{V} - T\left(\int_{T_0}^{T} \frac{C_V}{T'}\, dT' + \nu R \ln(V - \nu b) + S_0\right) \\
&= \int_{T_0}^{T} C_V \left(1 - \frac{T}{T'}\right) dT' - \frac{a\nu^2}{V} - \nu RT \ln(V - \nu b) + F_0
\end{aligned}$$

5.3

由范德瓦尔斯气体方程可知:

$$pV = \left(\frac{\nu RT}{V - \nu b} - \frac{a\nu^2}{V^2}\right) V = \frac{\nu RTV}{V - \nu b} - \frac{a\nu^2}{V}$$

则自由焓为:

$$
\begin{aligned}
G(T,V) = F + pV &= \int_{T_0}^{T} C_V \left(1 - \frac{T}{T'}\right) dT' - \frac{a\nu^2}{V} - \nu RT\ln(V-\nu b) + F_0 + pV \\
&= \int_{T_0}^{T} C_V \left(1 - \frac{T}{T'}\right) dT' + \frac{\nu RTV}{V-nb} - \frac{2a\nu^2}{V} - \nu RT\ln(V-\nu b) + G_0
\end{aligned}
$$