统计力学第二次作业

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2019 年 3 月 10 日

2.2

$$\left(\frac{\partial U}{\partial V}\right)_T = R\frac{\partial p}{\partial T} - p = Tf(v) - p = 0$$

$\square$

2.3

(a)

$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p = 0 \implies \mathrm{d}S = -\frac{V}{T}\mathrm{d}p$, 由于 $\frac{V}{T} > 0$, 当 $\mathrm{d}p > 0$, $\mathrm{d}S < 0$, 即 $\left(\frac{\partial S}{\partial p}\right)_H < 0$.

(b)

$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V = 0 \implies \mathrm{d}S = \frac{p}{T}\mathrm{d}V$, 由于 $\frac{p}{T} > 0$, 当 $\mathrm{d}V > 0$, $\mathrm{d}S > 0$, 即 $\left(\frac{\partial S}{\partial V}\right)_U > 0$.

$\square$

2.4

$$\left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T = 0 \implies \left(\frac{\partial U}{\partial p}\right)_T = 0$$

$\square$

2.5

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

由于 $\frac{C_p}{T}>0$, $\left(\frac{\partial S}{\partial V}\right)_p$ 与 $\left(\frac{\partial T}{\partial V}\right)_p$ 正负相同.

2.6

$$T\mathrm{d}S=C_V\mathrm{d}T+\left(\frac{\partial p}{\partial T}\right)_T\frac{\mathrm{d}V}{T}$$

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

$$\implies \mathrm{d}T=-\frac{T}{C_V}\frac{\alpha}{\kappa_T}\mathrm{d}V$$

当 $T,C_V,\kappa_T>0,\alpha,\mathrm{d}V<0$, 可以得到 $T<0$.

2.7

$$\mathrm{d}S=\frac{C_p}{T}\mathrm{d}T+\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}p=0\implies\left(\frac{\partial T}{\partial p}\right)_S=\frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p}$$

$$\mathrm{d}H=C_p\mathrm{d}T+\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p=0\implies\left(\frac{\partial T}{\partial p}\right)_H=\frac{-V+T\left(\frac{\partial V}{\partial T}\right)_p}{C_p}$$

$$\implies\left(\frac{\partial T}{\partial p}\right)_S-\left(\frac{\partial T}{\partial p}\right)_H=\frac{V}{C_p}>0$$

□

2.8

根据 $H=U(T)+pV$, H 仅为 T 的函数, 即 $\frac{\partial H}{\partial p}=V-T\left(\frac{\partial V}{\partial T}\right)_p=0$, 代入 $\left(\frac{\partial V}{\partial T}\right)_p=\frac{f'(T)}{p}$, $V=\frac{T}{p}f'(T)\implies f(T)=Tf'(T)\implies f(T)=CT$. 即 $pv=CT$.

2.9

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

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

积分可得 C_V, C_p. 理想气体 $\frac{\partial^2 p}{\partial T^2} = \frac{\partial^2 V}{\partial T^2} = 0$,

$$C_V = C_V^0 + T\int_{V_0}^{V}\left(\frac{\partial^2 p}{\partial T^2}\right)\mathrm{d}V = C_V^0 + C_1 T$$

$$C_p = C_p^0 - T\int_{p_0}^{p}\left(\frac{\partial^2 V}{\partial T^2}\right)\mathrm{d}p = C_p^0 + C_2 T$$

式中 C_V^0, C_p^0, C_1, C_2 为常数, 即 C_V, C_p 只与 T 相关.

□

2.13

$F = U - TS$, 当 T 不变, $F = \int dF = -\int \text{đ}W = -\int(-Ax)\,\mathrm{d}x = F(T,0) + \frac{1}{2}Ax^2$.
$S = -\frac{\partial F}{\partial T} = \frac{\mathrm{d}[-F(T,0)]}{\mathrm{d}T} - \frac{x^2}{2}\frac{\mathrm{d}A}{\mathrm{d}T} = S(T,0) - \frac{x^2}{2}\frac{\mathrm{d}A}{\mathrm{d}T}$.
$U = F + TS = F(T,0) + TS(T,0) + \frac{1}{2}\left(A - T\frac{\mathrm{d}A}{\mathrm{d}T}\right)x^2 = U(T,0) + \frac{1}{2}\left(A - T\frac{\mathrm{d}A}{\mathrm{d}T}\right)x^2$.

□