Problem 2.2. 设一物质的物态方程具有以下的形式：

$$p = f(v)T$$

试证明其内能与体积无关。

Solution:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = Tf(v) - f(v)T = 0 \tag{1}$$

故其内能与体积无关。 □

Problem 2.3. 求证：（a）$\left(\frac{\partial S}{\partial p}\right)_H < 0$；（b）$\left(\frac{\partial S}{\partial V}\right)_U > 0$.

Solution:
（a）焓的全微分

$$dH = TdS + Vdp \tag{2}$$

令$dH = 0$，得

$$\left(\frac{\partial S}{\partial p}\right)_H = -\frac{V}{T} < 0 \tag{3}$$

（b）内能的全微分

$$dU = TdS - pdV \tag{4}$$

令$dU = 0$，得

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T} > 0 \tag{5}$$

□

Problem 2.6. 试证明在相同的压强降落下，气体在准静态绝热膨胀中的温度降落大于在节流过程中的温度降落。
(提示：证明$\left(\frac{\partial T}{\partial p}\right)_S - \left(\frac{\partial T}{\partial p}\right)_H > 0$)

Solution: 将熵视为温度T和压强p的函数

$$S = S(T, p) \tag{6}$$

熵的全微分

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \tag{7}$$

令$S = 0$，得

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} \tag{8}$$

根据定压热容量表达式

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{9}$$

有

$$\left(\frac{\partial T}{\partial p}\right)_S=-\frac{T\left(\frac{\partial S}{\partial p}\right)_T}{C_p} \tag{10}$$

焓的全微分

$$dH=\left(\frac{\partial H}{\partial T}\right)_p dT+\left(\frac{\partial H}{\partial p}\right)_T dp \tag{11}$$

令$dH=0$，得

$$\left(\frac{\partial T}{\partial p}\right)_H=-\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \tag{12}$$

根据定压热容量的定义

$$C_p=\left(\frac{\partial H}{\partial T}\right)_p \tag{13}$$

和温度保持不变时焓随压强的变化率与物态方程的关系

$$\left(\frac{\partial H}{\partial p}\right)_T=V-\left(\frac{\partial V}{\partial T}\right)_p \tag{14}$$

有

$$\left(\frac{\partial T}{\partial p}\right)_H=\frac{\left(\frac{\partial V}{\partial T}\right)_p-V}{C_p} \tag{15}$$

从而

$$\left(\frac{\partial T}{\partial p}\right)_S-\left(\frac{\partial T}{\partial p}\right)_H=\frac{V}{C_p}>0 \tag{16}$$

故在相同的压强降落下，气体在准静态绝热膨胀中的温度降落大于在节流过程中的温度降落。 □

Problem 2.7. 实验发现，一气体的压强p与比体积v的乘积及内能密度u都只是温度T的函数，即

$$pV=f(T),\quad U=U(T)$$

试根据热力学理论，讨论该气体的物态方程可能具有什么形式。

Solution: 设气体质量为m，则$V=mv$，从而

$$pV=p\cdot mv=mf(T) \tag{17}$$

气体内能

$$U=Vu(T) \tag{18}$$

一方面，气体内能在恒温下关于体积V的偏导

$$\left(\frac{\partial U}{\partial V}\right)_T=u(T) \tag{19}$$

另一方面，温度保持不变时内能随体积的变化率与物态方程的关系

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T =&T\left(\frac{\partial p}{\partial T}\right)_V - p = T\left(\frac{\partial\left(\frac{mf(T)}{V}\right)}{\partial T}\right)_V - \frac{mf(T)}{V}\\ =&\frac{mT}{V}\frac{df(T)}{dT} - \frac{mf(T)}{V}\end{aligned} \tag{20}$$

故

$$u(T) = \frac{mT}{V}\frac{df(T)}{dT} - \frac{mf(T)}{V} \tag{21}$$

内能密度在恒温下关于体积V的偏导

$$\left(\frac{\partial u(T)}{\partial V}\right)_T = -\frac{mT}{V^2}\frac{df(T)}{dT} + \frac{mf(T)}{V^2} = 0 \tag{22}$$

$$\Longrightarrow \frac{df(T)}{f(T)} = \frac{dT}{T} \tag{23}$$

$$\Longrightarrow \ln f(T) = \ln T + \ln C \tag{24}$$

$$\Longrightarrow pV = mCT \tag{25}$$

□

Problem 2.9. 试证明

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

并由此导出

$$C_V = C_V^0 + T\int_{V_0}^V \left(\frac{\partial^2 p}{\partial T^2}\right)_V dV$$
$$C_p = C_p^0 - T\int_{p_0}^p \left(\frac{\partial^2 V}{\partial T^2}\right)_p dp$$

根据以上两式证明，理想气体的定容热容量和定压热容量只是温度T的函数。

Solution: 等容热容

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{26}$$

C_V在恒温条件下关于体积V的偏导

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T = T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V \tag{27}$$

根据麦氏关系$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V \tag{28}$$

在恒温条件下方程两边同对体积V积分，得

$$C_V = C_V^0 + T\int_{V_0}^{V}\left(\frac{\partial^2 p}{\partial T^2}\right)_V dV \tag{29}$$

等压热容

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{30}$$

C_p在恒温条件下关于压强p的偏导

$$\left(\frac{\partial C_p}{\partial p}\right)_T = T\left(\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_p\right)_T = T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_T\right)_p \tag{31}$$

根据麦氏关系$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{32}$$

在恒温条件下方程两边同对压强p积分，得

$$C_p = C_p^0 - T\int_{p_0}^{p}\left(\frac{\partial^2 V}{\partial T^2}\right)_p dp \tag{33}$$

理想气体物态方程

$$pV = nRT \tag{34}$$

从而

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0 \tag{35}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = 0 \tag{36}$$

故理想气体的定容热容量和定压热容量只是温度T的函数。 □

Problem 2.13. X射线衍射实验发现，橡皮带未被拉紧时具有无定型结构，当受张力而被拉伸时，具有晶体结构。这一事实表明橡皮带具有大的分子链。（a）试讨论橡皮带在等温过程中被拉伸时它的熵是增加还是减少；（b）试证明它的膨胀系数$\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_F$是负的。

Solution:

（a）橡皮带拉紧后由无定型结构转变为晶体结构，有序程度增加，而熵是刻画系统无序程度的状态函数，因此橡皮带在等温过程中被拉伸时它的熵减少。

（b）橡皮带自由能的全微分（为与题设中的橡皮筋拉力F相区分，用字母f表示）

$$df = -SdT + FdL \tag{37}$$

从而

$$\left(\frac{\partial f}{\partial T}\right)_L = -S \tag{38}$$

$$\left(\frac{\partial f}{\partial L}\right)_T = F \tag{39}$$

考虑到偏导数的次序可以交换

$$\left(\frac{\partial}{\partial L}\left(\frac{\partial f}{\partial T}\right)_L\right)_T = -\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial f}{\partial L}\right)_T\right)_L = \left(\frac{\partial F}{\partial T}\right)_L \tag{40}$$

根据（a）中结论

$$\left(\frac{\partial S}{\partial L}\right)_T < 0 \tag{41}$$

故

$$\left(\frac{\partial F}{\partial T}\right)_L > 0 \tag{42}$$

根据链式关系

$$\left(\frac{\partial L}{\partial T}\right)_F = \frac{-1}{\left(\frac{\partial T}{\partial F}\right)_L\left(\frac{\partial F}{\partial L}\right)_T} = \frac{-\left(\frac{\partial F}{\partial T}\right)_L}{\left(\frac{\partial F}{\partial L}\right)_T} \tag{43}$$

根据生活常识，橡皮带受拉力伸长

$$\left(\frac{\partial F}{\partial L}\right)_T > 0 \tag{44}$$

因此

$$\left(\frac{\partial L}{\partial T}\right)_F = \frac{-\left(\frac{\partial F}{\partial T}\right)_L}{\left(\frac{\partial F}{\partial L}\right)_T} < 0 \tag{45}$$

故它的膨胀系数

$$\alpha = \frac{1}{L}(\frac{\partial L}{\partial T})_F < 0 \tag{46}$$

□

Problem 2.14. 假设太阳是黑体，根据下列数据求太阳表面的温度。
单位时间内透射到地球大气层外单位面积上的太阳辐射能量为$1.35 \times 10^3 \mathrm{J}\cdot\mathrm{m}^{-2}\cdot\mathrm{s}^{-1}$（该值称为太阳常数），太阳的半径为$6.955\times10^8\mathrm{m}$，太阳与地球的平均距离为$1.495\times10^{11}\mathrm{m}$。

Solution: 太阳的总辐射功率为

$$P = J_{u1}\cdot 4\pi r^2 = 1.35\times10^3\mathrm{J}\cdot\mathrm{m}^{-2}\cdot\mathrm{s}^{-1}\times 4\pi(1.495\times10^{11}\mathrm{m})^2 = 3.79\times10^{26}\mathrm{W} \tag{47}$$

太阳作为一个黑体，其表面的辐射通量密度

$$J_u = \frac{P}{4\pi R^2} = \frac{3.79\times10^{26}\mathrm{W}}{4\pi(6.955\times10^8\mathrm{m})^2} = 6.24\times10^7\mathrm{W}\cdot\mathrm{m}^2 \tag{48}$$

根据斯特藩-玻尔兹曼定律，太阳表面的温度

$$T = \sqrt[4]{\frac{J_u}{\sigma}} = \sqrt[4]{\frac{6.24\times 10^7 \mathrm{W}\cdot\mathrm{m}^2}{5.669\times 10^{-8}\mathrm{W}\cdot\mathrm{m}^{-2}\cdot\mathrm{K}^{-4}}} = 5.76\times 10^3 K \tag{49}$$

□

Problem 2.18. 试证明磁介质C_H与C_M之差等于

$$C_H - C_M = \mu_0 T\left(\frac{\partial H}{\partial T}\right)_M^2\left(\frac{\partial M}{\partial H}\right)_T$$

Solution: 将磁介质内能视为温度T和总磁矩m的函数

$$U = U(T, m) \tag{50}$$

磁介质内能的全微分

$$dU = \left(\frac{\partial U}{\partial T}\right)_m dT + \left(\frac{\partial U}{\partial m}\right)_T dm \tag{51}$$

又可写成

$$dU = TdS + \mu_0 H dm \tag{52}$$

由熵的全微分表达式

$$dS = \left(\frac{\partial S}{\partial T}\right)_m dT + \left(\frac{\partial S}{\partial m}\right)_T dm \tag{53}$$

可得

$$dU = T\left(\frac{\partial S}{\partial T}\right)_m dT + \left[T\left(\frac{\partial S}{\partial m}\right)_T + \mu_0 H\right] dm \tag{54}$$

故

$$C_m = \left(\frac{\partial U}{\partial T}\right)_m = T\left(\frac{\partial S}{\partial T}\right)_m \tag{55}$$

将磁介质的焓视为温度T和磁场强度H的函数（为与磁场强度H相区分，焓用字母h表示）

$$h = h(T, H) \tag{56}$$

磁介质焓的全微分

$$dh = \left(\frac{\partial H}{\partial T}\right)_H dT + \left(\frac{\partial h}{\partial H}\right)_T dH \tag{57}$$

又可写成

$$dh = TdS + \mu_0 m dH \tag{58}$$

由熵的全微分表达式

$$dS = \left(\frac{\partial S}{\partial T}\right)_H dT + \left(\frac{\partial S}{\partial H}\right)_T dH \tag{59}$$

可得

$$dh = T\left(\frac{\partial S}{\partial T}\right)_H dT + \left[T\left(\frac{\partial S}{\partial H}\right)_T + \mu_0 m\right] dH \tag{60}$$

故

$$C_H = \left(\frac{\partial h}{\partial T}\right)_H = T\left(\frac{\partial S}{\partial T}\right)_H \tag{61}$$

$$\Longrightarrow C_H - C_m = T\left(\frac{\partial S}{\partial T}\right)_H - T\left(\frac{\partial S}{\partial T}\right)_m \tag{62}$$

将磁介质的熵视为温度T和磁场强度H的函数

$$S = S(T,H) = S(T, m(T,H)) \tag{63}$$

磁介质熵在恒定磁场下关于温度T的偏导

$$\left(\frac{\partial S}{\partial T}\right)_H = \left(\frac{\partial S}{\partial T}\right)_m + \left(\frac{\partial S}{\partial m}\right)_T\left(\frac{\partial m}{\partial T}\right)_H \tag{64}$$

从而

$$C_H - C_m = T\left(\frac{\partial S}{\partial m}\right)_T\left(\frac{\partial m}{\partial T}\right)_H = T\left(\frac{\partial S}{\partial m}\right)_T\left(\frac{\partial m}{\partial T}\right)_H \tag{65}$$

利用麦氏关系$\left(\frac{\partial S}{\partial m}\right)_T = -\mu_0\left(\frac{\partial H}{\partial T}\right)_m$

$$C_H - C_m = -\mu_0 T\left(\frac{\partial H}{\partial T}\right)_m\left(\frac{\partial m}{\partial T}\right)_H \tag{66}$$

根据链式关系

$$\left(\frac{\partial m}{\partial T}\right) = \frac{-1}{\left(\frac{\partial T}{\partial H}\right)_m\left(\frac{\partial H}{\partial m}\right)_T} = -\left(\frac{\partial H}{\partial T}\right)_m\left(\frac{\partial m}{\partial H}\right)_T \tag{67}$$

故

$$C_H - C_m = -\mu_0 T\left(\frac{\partial H}{\partial T}\right)_m^2\left(\frac{\partial m}{\partial H}\right)_T \tag{68}$$

□

Problem 2.20. 已知超导体的磁感应强度$B = \mu_0(H+M) = 0$，求证：
（a）C_M与M无关，只是T的函数，其中C_M是在磁化强度M保持不变的热容量。
（b）$U = \int C_M dT - \frac{\mu_0 M^2}{2} + U_0$
（c）$S = \int \frac{C_M}{T} dT + S_0$

Solution:
（a）超导体的热容量

$$C_M = T\left(\frac{\partial S}{\partial T}\right)_M \tag{69}$$

热容量在恒温下关于磁化强度M的偏导

$$\left(\frac{\partial C_M}{\partial M}\right)_T = \left(\frac{\partial}{\partial M}\left(T\frac{\partial S}{\partial T}\right)_M\right)_T = T\left(\frac{\partial}{\partial M}\left(\frac{\partial S}{\partial T}\right)_M\right)_T = T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial M}\right)_T\right)_M \tag{70}$$

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根据磁介质的麦氏关系$\left(\frac{\partial S}{V\partial M}\right)_T=-\mu_0\left(\frac{\partial H}{\partial T}\right)_M$

$$\left(\frac{\partial C_M}{\partial M}\right)_T=-\mu_0TV\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial T}\right)_T\right)_M \tag{71}$$

由

$$B=\mu_0(H+M)=0 \tag{72}$$

得

$$H=-M\Longrightarrow\left(\frac{\partial H}{\partial T}\right)_M=0 \tag{73}$$

从而

$$\left(\frac{\partial C_M}{\partial M}\right)_T=0 \tag{74}$$

故C_M与M无关，只是T的函数。

（b）由内能的全微分

$$dU=TdS+\mu_0Hdm=TdS-\mu_0VMdM \tag{75}$$

得

$$\left(\frac{\partial U}{\partial M}\right)_T=-\mu_0VM \tag{76}$$

内能的全微分又可写作

$$dU=\left(\frac{\partial U}{\partial T}\right)_M dT+\left(\frac{\partial U}{\partial M}\right)_M dM=C_MdT-\mu_0VM \tag{77}$$

积分即得

$$U=\int C_MdT-\frac{\mu_0VM^2}{2}+U_0 \tag{78}$$

（c）超导体熵的全微分

$$dS=\left(\frac{\partial S}{\partial T}\right)_M dT+\left(\frac{\partial S}{\partial m}\right)_T dm \tag{79}$$

由超导体的热容量

$$C_M=T\left(\frac{\partial S}{\partial T}\right)_M \tag{80}$$

得

$$\left(\frac{\partial S}{\partial T}\right)_M=\frac{C_M}{T} \tag{81}$$

再结合超导体的麦氏关系$\left(\frac{\partial S}{\partial m}\right)_T=\mu_0\left(\frac{\partial H}{\partial T}\right)_M$，得

$$dS=\frac{C_M}{T}+\mu_0\left(\frac{\partial H}{\partial T}\right)_M \tag{82}$$

其中

$$B=\mu_0(H+M)=0\Longrightarrow H=-M\Longrightarrow\left(\frac{\partial H}{\partial T}\right)_M=0 \tag{83}$$

故积分得

$$S=\int\frac{C_M}{T}dT+S_0 \tag{84}$$

□