1.1, 1.2, 1.3, 1.4, 1.5, 1.6

1.1

解:

理想气体物态方程 pV = nRT,代入定义即得

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \frac{nR}{p} = \frac{1}{T}$$

$$\beta = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V = \frac{1}{p} \frac{nR}{V} = \frac{1}{T}$$

$$\kappa_T = -rac{1}{V}\left(rac{\partial V}{\partial p}
ight)_T = rac{1}{V}rac{nRT}{p^2} = rac{1}{p}$$

1.2

证明:

由于 V=V(p,T),有全微分

$$\mathrm{d}V = \left(rac{\partial V}{\partial T}
ight)_p \mathrm{d}T + \left(rac{\partial V}{\partial p}
ight)_T \mathrm{d}p$$

又由于

$$lpha = rac{1}{V} \left(rac{\partial V}{\partial T}
ight)_p, \quad \kappa_T = -rac{1}{V} \left(rac{\partial V}{\partial p}
ight)_T$$

故

$$rac{\mathrm{d}V}{V} = lpha \mathrm{d}T - \kappa_T \mathrm{d}p$$

积分即得

$$\ln V = \int (lpha \mathrm{d}T - \kappa_T \mathrm{d}p)$$

若 $\alpha = \frac{1}{T}, \kappa_T = \frac{1}{p}$,则

$$\ln V = \int (lpha \mathrm{d}T - \kappa_T \mathrm{d}p) = \ln V = \int \left(rac{1}{T}\mathrm{d}T - rac{1}{p}\mathrm{d}p
ight) = \ln T - \ln p + C$$

即

$$\frac{pV}{T} = C$$

1.3

证明:

根据上题结论,我们有

$$rac{\mathrm{d}V}{V} = lpha \mathrm{d}T - \kappa_T \mathrm{d}p$$

从 $(T,p)=(T_0,0)$ 积分到 (T,p)=(T,p),得

$$V(T,p) = V(T_0,p) \exp(lpha(T-T_0) - \kappa_T p) = V_0(T_0,p)[1 + lpha(T-T_0) - \kappa_T p]$$

上式中利用了 $lpha(T-T_0), \kappa_T p \ll 1$

1.4

解:

(1)

根据上题结论,

$$V(T,p')=V_0(T_0,p)[1+lpha(T-T_0)-\kappa_T\Delta p]$$

因为
$$V(T,p')=V_0(T_0,p)$$
,即 $lpha(T-T_0)-\kappa_T\Delta p=0$ 。所以

$$\Delta p = rac{lpha}{\kappa_T} (T - T_0) = rac{4.85 imes 10^{-5}}{7.8 imes 10^{-7}} imes 10 = 622 \, ext{atm}$$

(2)

根据上题结论,

$$rac{\Delta V}{V} = lpha \Delta T - \kappa_T \Delta p = 4.85 imes 10^{-5} imes 10 - 7.8 imes 10^{-7} imes 100 = 4.07 imes 10^{-4}$$

即铜块体积增加 4.07×10^{-4} 倍。

1.5

证明:

金属丝两端固定,L 为常数。

根据物态方程 $f(\mathcal{J}, L, T) = 0$, 得偏导关系

$$\left(\frac{\partial \mathscr{J}}{\partial L}\right)_T \left(\frac{\partial L}{\partial T}\right)_{\mathscr{J}} \left(\frac{\partial T}{\partial \mathscr{J}}\right)_L = -1$$

故

$$\left(\frac{\partial \mathscr{J}}{\partial T}\right)_{L} = -\left(\frac{\partial \mathscr{J}}{\partial L}\right)_{T} \left(\frac{\partial L}{\partial T}\right)_{\mathscr{J}} = -EA\alpha_{l}$$

在温度变化不大时, $\alpha_l = \alpha$ 视为常数。则

$$\Delta \mathscr{J} = -EAlpha(T_2 - T_1)$$

1.6

证明:

有物态方程 $\mathscr{J}=\mathscr{J}(L,T)$

(a)

等温弹性模量

$$E = rac{L}{A} \left(rac{\partial \mathscr{J}}{\partial L}
ight)_T = rac{L}{A} bT \left(rac{1}{L_0} + rac{2L_0^2}{L^3}
ight) = rac{bT}{A} \left(rac{L}{L_0} + rac{2L_0^2}{L^2}
ight)$$

(b)

线膨胀系数

$$\alpha_l = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_{\mathscr{J}} = -\frac{1}{L} \left(\frac{\partial \mathscr{J}}{\partial T} \right)_L / \left(\frac{\partial \mathscr{J}}{\partial L} \right)_T = -\frac{1}{T} \frac{L/L_0 - L_0^2/L^2}{L/L_0 + 2L_0^2/L^2} + \frac{1}{L_0} \frac{\mathrm{d}L_0}{\mathrm{d}T}$$

3.20

1.7, 1.8, 1.9, 1.10

1.7

证明:

将该部分气体作为系统,过程中来不及热量交换,Q=0。在大气将气体等压压入盒中时,大气对系统做功

$$W = p_0 V_0$$

根据热力学第一定律,系统内能

$$U - U_0 = W = p_0 V_0$$

若气体是理想气体, U = U(T), 那么

$$U-U_0 = C_V(T-T_0) = rac{nR}{\gamma-1}(T-T_0)$$

又由理想气体状态方程 $p_0V_0=nRT_0, p_0V=nRT$,得

$$T = \gamma T_0, V = \gamma V_0$$

1.8

证明:

多方过程 $pV^n=C$ 。理想气体 pV=nRT,故 $TV^{n-1}=C'$

$$\left(\frac{\partial V}{\partial T}\right)_n = -\frac{V}{(n-1)T}$$

$$C_V = \left(rac{\partial U}{\partial T}
ight)_n = rac{nR}{\gamma - 1}$$

得到热容

$$C_n = \lim_{\Delta T o 0} \left(rac{\Delta Q}{\Delta T}
ight)_n = \left(rac{\partial U}{\partial T}
ight)_n + p\left(rac{\partial V}{\partial T}
ight)_n = C_V - rac{pV}{(n-1)T} = rac{n-\gamma}{n-1}C_V$$

1.9

证明:

根据热力学第一定律,

$$C_V dT = C_n dT - p dV$$

由状态方程 pV=
u RT,且 $C_p-C_V=
u R$,得

$$(C_n-C_V)rac{\mathrm{d}T}{T}=(C_p-C_V)rac{\mathrm{d}V}{V},rac{\mathrm{d}p}{p}+rac{\mathrm{d}V}{V}=rac{\mathrm{d}T}{T}$$

记 $n=(C_n-C_p)/(C_n-C_V)$,上式消去 T 项,得到

$$\frac{\mathrm{d}p}{p} + n\frac{\mathrm{d}V}{V} = 0$$

积分得

$$pV^n = C$$

这是一个多方过程。

1.10

证明:

引入比体积 v=1/
ho。在绝热过程中,气体

$$\left(\frac{\partial p}{\partial v}\right)_S = -\gamma \frac{p}{v}$$

$$a^2 = \left(rac{\partial p}{\partial
ho}
ight)_S = -v^2 \left(rac{\partial p}{\partial v}
ight)_S = \gamma p v$$

又由理想气体状态方程, pmv = nRT。

单位质量的内能和焓

$$u=u_0+\int c_V \mathrm{d}T/m=u_0+rac{nRT}{(\gamma-1)m}=u_0+rac{a^2}{\gamma(\gamma-1)}$$

$$h=h_0+\int c_p \mathrm{d}T/m=h_0+rac{\gamma nRT}{(\gamma-1)m}=h_0+rac{a^2}{\gamma-1}.$$

3.22

1.11, 1.12, 1.13

1.11

讨论 z 处的空气。由于 $p(z+\mathrm{d}z)=p(z)+\rho(z)g\mathrm{d}z$,得到

$$\frac{\mathrm{d}p}{\mathrm{d}z} = -\rho(z)g$$

又由物态方程,

$$prac{m}{
ho}=nRT\Rightarrow
ho(z)=rac{M}{RT}p(z)$$

又绝热过程中

$$\left(\frac{\partial T}{\partial p}\right)_{S} = \frac{\gamma - 1}{\gamma} \frac{T}{p}$$

代入,得

$$\frac{\mathrm{d}T}{\mathrm{d}z} = \left(\frac{\partial T}{\partial p}\right)_S \frac{\mathrm{d}p}{\mathrm{d}z} = -\frac{\gamma - 1}{\gamma} \frac{Mg}{R}$$

大气中, $\gamma = 1.41, M = 29$ 。故

$$\frac{\mathrm{d}T}{\mathrm{d}z} = -10\,\mathrm{K}\cdot\mathrm{km}^{-1}$$

理想气体在准静态绝热过程中, $C_V \mathrm{d}T + p \mathrm{d}V = 0$ 。根据

$$C_p - C_V = nR, C_p/C_V = \gamma \Rrightarrow C_V = rac{1}{\gamma - 1} nR$$

故

$$\frac{1}{\gamma - 1} \frac{\mathrm{d}T}{T} + \frac{\mathrm{d}V}{V} = 0$$

定义

$$\ln F(T) = \int \frac{\mathrm{d}T}{(\gamma - 1)T}$$

积分得到

$$F(T)V = C$$

1.13

卡诺循环中,

$$Q_1 = RT_1 \ln rac{V_2}{V_1}, Q_2 = RT_2 \ln rac{V_3}{V_4}$$

由于绝热过程中,有

$$F(T_1)V_2 = F(T_2)V_3, F(T_2)V_4 = F(T_1)V_1$$

消去温度函数得到 $V_2/V_1=V_3/V_4$ 。故 $Q_1/Q_2=T_1/T_2$ 。效率

$$\eta=rac{W}{Q_1}=1-rac{T_2}{T_1}$$

1.14

1.14

证明:

假设有两条绝热线相交于点X。现做一等温线,交两条绝热线于点A,B。现在我们让一个热机工作在ABXA的正循环下。此时系统从单一热源T吸热,并对外做功,且回到了原来的状态。这一点违反了热力学第二定律。故两条绝热线不相交。

3.29

1.15, 1.16, 1.17, 1.18, 1.19

1.15

证明:

根据克劳修斯不等式,有

$$\oint \frac{\mathrm{d}Q}{T} \leqslant 0$$

若将 đQ 重定义为吸热/放热,分别为 Q_j,Q_k 。那么

$$\sum_j rac{Q_j}{T_j} \leqslant \sum_k rac{Q_k}{T_k}$$

在热机吸收热源最高温度为 T_1 ,最低热源温度为 T_2 。那么

$$rac{1}{T_1}\sum_j Q_j \leqslant \sum_j rac{Q_j}{T_j} \leqslant \sum_k rac{Q_k}{T_k} \leqslant rac{1}{T_2}\sum_k Q_k$$

记总吸热/放热为 Q_1,Q_2 ,则 $Q_1/T_1 \leqslant Q_2/T_2$ 。故

$$\eta=1-rac{Q_2}{Q_1}\leqslant 1-rac{T_2}{T_1}$$

证明:

等压过程中, $S=C_p\ln T-nR\ln p+S_0$,故

$$(\Delta S)_p = C_p \ln rac{T_2}{T_1}$$

等容过程中, $S = C_V \ln T + nR \ln V + S_0$, 故

$$(\Delta S)_V = C_V \ln \frac{T_2}{T_1}$$

所以

$$\frac{(\Delta S)_p}{(\Delta S)_V} = \frac{C_p}{C_V} = \gamma$$

1.17

解:

水分别经历 $0^{\circ}C - 100^{\circ}C$ 的每个温度,故

$$\Delta_{7\! ext{K}} = \int_{T_0}^{T_1} rac{mc\mathrm{d}T}{T} = mc\lnrac{T_1}{T_0} = 4.18 imes 10^3 imes \lnrac{373.15}{273.15} = 1304\,\mathrm{J\cdot K^{-1}}$$

热源保持温度不变, 故

$$\Delta_{ar{\mathbb{R}}} = -rac{mc\Delta T}{T} = rac{4.18 imes 10^3 imes 100}{373.15} = -1120\,\mathrm{J\cdot K^{-1}}$$

故系统总熵变

$$\Delta_{\ddot{\mathbb{R}}} = \Delta_{7\!\!K} + \Delta_{\ddot{\mathbb{R}}} = 1304 - 1120 = 184\,J\cdot K^{-1}$$

若要加热水使得体系没有熵增,应该采用可逆过程,用无穷多个热源依次给水加热,使得水温升高。

1.18

解:

电阻产生焦耳热

$$Q = I^2 Rt = 10^2 \times 25 \times 1 = 2500 \,\mathrm{J}$$

(a)

电阻器保持 $27\,^{\circ}\mathrm{C}$ 温度不变,电阻仍处在初始状态,故熵不变, $\Delta S=0$ 。

(b)

焦耳热全部被电阻吸收,

$$T' = T_0 + rac{Q}{mc_p} = 300.15 + rac{2500}{10 imes 0.84} = 597.77 \, \mathrm{K}$$

故熵增

$$\Delta S = \int_{T_0}^{T'} rac{m c_p \mathrm{d} T}{T} = m c_p \ln rac{T'}{T_0} = 0.84 imes 10 imes \ln rac{597.77}{300.15} = 5.79 \, \mathrm{J} \cdot \mathrm{K}^{-1}$$

1.19

解:

设杆长为 L,单位长度热容量为 c。在杆方向上建坐标系,中心处为原点。初始温度分布为

$$T(x)=rac{T_1+T_2}{2}+rac{T_2-T_1}{L}x,\quad -rac{L}{2}\leqslant x\leqslant rac{L}{2}$$

在 x 处长度为 $\mathrm{d}x$ 的杆元熵变为

$$\mathrm{d}S(x) = \int_{T(x)}^{T(0)} rac{c\mathrm{d}x\,\mathrm{d}T}{T} = c\mathrm{d}x\lnrac{T(0)}{T(x)}$$

故全杆熵增为

$$\Delta S = \int_{-L/2}^{L/2} c dx \ln \frac{T(0)}{T(x)} = c \int_{-L/2}^{L/2} \left(\ln \frac{T_1 + T_2}{2} - \ln \left(\frac{T_1 + T_2}{2} + \frac{T_2 - T_1}{L} x \right) \right) dx$$

$$= cL \ln \frac{T_1 + T_2}{2} - \frac{c}{(T_2 - T_1)/L} (T_2 \ln T_2 - T_1 \ln T_1 - T_2 + T_1)$$

$$= C \left(\ln \frac{T_1 + T_2}{2} - \frac{T_2 \ln T_2 - T_1 \ln T_1}{T_2 - T_1} + 1 \right)$$

4.3

1.20, 1.21, 1.22, 1.23

在固定压强下,过冷液体和固体在 T_0-T_1 的熵变,以及相变的熵变分别为

$$\Delta S_l = \int_{T_0}^{T_1} rac{C_l \mathrm{d}T}{T} = C_l \ln rac{T_1}{T_0}, \; \Delta S_g = \int_{T_0}^{T_1} rac{C_g \mathrm{d}T}{T} = C_g \ln rac{T_1}{T_0} \ \Delta S_{lg} = rac{Q_0}{T_0}$$

故

$$\Delta S = \Delta S_l + \Delta S_{lg} - \Delta S_g = rac{Q_0}{T_0} + (C_s - C_l) \ln rac{T_0}{T_1}$$

1.21

证明:

用Q'表示热机在热源处的总放热。根据热力学第一定律,有

$$Q_1 = Q_2 + W$$

过程中,物体和热源熵变分别为 $S_2-S_1,Q'/T_2$ 。热机经历可逆循环回到初始状态,故熵变为0。根据熵增原理,

$$\Delta S = S_2 - S_1 + Q'/T_2 \geqslant 0$$

故

$$W\leqslant Q-T_2(S_1-S_2)$$

1.22

证明:

制冷机回到初始状态,熵不变。而两个物体

$$\Delta S_1 = C_p \ln rac{T_1}{T_i} \ \Delta S_2 = C_p \ln rac{T_2}{T_i}$$

$$\Delta S = \Delta S_1 + \Delta S_2 \geqslant 0$$

得

$$T_1T_2/T_i^2\geqslant 1$$

制冷机

$$W = Q_2 - Q_1 = C_p(T_1 - T_2 - 2T_i) \geqslant C_p\left(rac{T_i^2}{T_2} + T_2 - 2T_i
ight)$$

1.23

解:

如图所示。

因为卡诺循环由两个绝热过程和两个等温过程构成,故在 T-S 图上为一个长方形。显然,系统在高温热源吸热 $Q_1=T_1(S_2-S_1)$,在低温热源放热 $Q_2=T_2(S_2-S_1)$ 。故卡诺热机的效率

$$\eta = 1 - rac{Q_2}{Q_1} = 1 - rac{T_2}{T_1}$$

4.10

2.1, 2.2, 2.3, 2.4, 2.5

2.1

证明:

由题意

$$\left(rac{\partial p}{\partial T}
ight)_V = C > 0 \Rightarrow p = f(V)T, \; f(V) > 0$$

故根据麦克斯韦关系,有

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = f(V) > 0$$

即在物质温度不变时,熵随着体积的增加而增加。

2.2

证明:

根据麦克斯韦关系,有

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

故内能与体积无关。

2.3

证明:

$$dH = TdS + Vdp = 0$$

故

$$\left(\frac{\partial S}{\partial p}\right)_{H} = -\frac{V}{T} < 0$$

同理,

$$dU = TdS - pdV = 0$$

故

$$\left(\frac{\partial S}{\partial V}\right)_{U} = \frac{p}{T} > 0$$

2.4

证明:

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

证明:

$$\left(\frac{\partial S}{\partial V}\right)_p = \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p = \frac{C_p}{T} \left(\frac{\partial T}{\partial V}\right)_p$$

其中 $C_p/T>0$ 。故前一项的正负取决于后一项的正负,即一个均匀物体在等压过程中熵随体积的增减取决于等压下温度随体积的增减。

4.12

2.8, 2.9, 2.10, 2.11, 2.12, 2.13, 2.14

2.8

解:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{T}{V}f'(T) - p = 0$$

故

$$Tf'(T) = f(T) \Rightarrow f(T) = CT$$

所以状态方程 pV = CT。

2.9

证明:

$$C_V = \left(rac{\partial U}{\partial T}
ight)_V = T\left(rac{\partial S}{\partial T}
ight)_V$$

故

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

积分后有

$$C_V = C_V^0 + T \int_{V_0}^V \left(rac{\partial^2 p}{\partial T^2}
ight)_V \mathrm{d}V$$

同理,有

$$\left(rac{\partial C_p}{\partial p}
ight)_T = T\left(rac{\partial^2 S}{\partial p \partial T}
ight) = -T\left(rac{\partial^2 V}{\partial T^2}
ight)_p$$

$$C_p = C_p^0 - T \int_{p_0}^p \left(rac{\partial^2 V}{\partial T^2}
ight)_p \mathrm{d}p$$

理想气体有 pV = nRT, 故

$$\left(rac{\partial^2 p}{\partial T^2}
ight)_V = \left(rac{\partial^2 V}{\partial T^2}
ight)_p = 0$$

所以 C_V, C_p 均只为 T 的函数。

2.10

证明:

范式气体

$$\left(p + rac{n^2a}{V^2}
ight)(V - nb) = nRT$$

由

$$\left(rac{\partial C_V}{\partial V}
ight)_T = T \left(rac{\partial^2 p}{\partial T^2}
ight)_V = 0$$

故范式气体的定容热容只是温度 T 的函数,与体积无关。

证明:

理想气体

$$U_m = \int C_{V,m} \mathrm{d}T + U_{m0}$$

$$S_m = \int rac{C_{V,m}}{T} \mathrm{d}T + R \ln V_m + S_{m0}$$

故

$$egin{aligned} F_m &= U_m - TS_m = \int C_{V,m} \mathrm{d}T + U_{m0} - T \int rac{C_{V,m}}{T} \mathrm{d}T - RT \ln V_m - TS_{m0} \ &= -T \int rac{\mathrm{d}T}{T^2} \int C_{V,m} \mathrm{d}T + U_{m0} - TS_{m0} - RT \ln V_{m0} \end{aligned}$$

2.12

解:

考虑 1mol 范式气体,特性函数

$$F_m = -S_m dT - p dV$$

故

$$\left(rac{\partial F_m}{\partial V_m}
ight)_T = -p = -rac{RT}{V_m-b} + rac{a}{V_m^2}$$

积分,得到

$$F_m(T,V_m) = -RT\ln(V_m-b) - rac{a}{V_m} + f(T)$$

我们有边界条件,即 $V_m o \infty$ 时回到理想气体,则

$$f(T) = \int C_{V,m} \mathrm{d}T + U_{m0} - T \int rac{C_{V,m}}{T} \mathrm{d}T - T S_{m0}$$

熵和内能

$$S_m = -\left(rac{\partial F_m}{\partial T}
ight)_V = \int rac{C_{V,m}}{T} \mathrm{d}T + R \ln(V_m - b) + S_{m0}$$

$$U_m = F_m + TS_m = \int C_{V,m} \mathrm{d}T - rac{a}{V_m} + U_{m0}$$

2.13

证明:

对于弹簧,有

$$dU = TdS - F_x dx \Rightarrow dF = -SdT - F_x dx$$

故

$$\left(\frac{\partial F}{\partial x}\right)_T = -F_x = Ax$$

积分得到

$$F(T,x)=F(T,0)+rac{1}{2}Ax^2$$

所以

$$S(T,x) = -\left(rac{\partial F}{\partial T}
ight)_x = S(T,0) - rac{x^2}{2}rac{\mathrm{d}A}{\mathrm{d}T}$$

$$U=F+TS=U(T,0)+rac{1}{2}\left(A-Trac{\mathrm{d}A}{\mathrm{d}T}
ight)x^2$$

2.14

解:

(a)

橡皮筋经过拉伸,从无定形结构变为晶体结构,即从无序度降低了,所以熵减小了。

(b) 证明:

橡皮筋的自由能

$$\mathrm{d}F = -S\mathrm{d}T + \mathscr{J}\mathrm{d}L$$

故

$$\left(\frac{\partial \mathscr{J}}{\partial T}\right)_{L} = -\left(\frac{\partial S}{\partial L}\right)_{T} > 0$$

所以膨胀系数

$$\alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_{\mathscr{J}} = -\frac{1}{L} \left(\frac{\partial L}{\partial \mathscr{J}} \right)_{T} \left(\frac{\partial \mathscr{J}}{\partial T} \right)_{L} < 0$$

4.17

2.15, 2.16, 2.17

2.15

解:

黑体辐射通量密度 $J_u = \sigma T^4$ 。由

$$J_u R_s^2 = J_s R_{se}^2$$

得

$$T = \left(rac{J_u}{\sigma}
ight)^{1/4} = \left(rac{J_s R_{se}^2}{\sigma R_s^2}
ight)^{1/4} = \left(rac{1.35 imes 10^3 imes (1.495 imes 10^{11})^2}{5.67 imes 10^{-8} imes (6.955 imes 10^8)^2}
ight)^{1/4} = 5760 \, {
m K}$$

2.16

解:

辐射场的熵 $S=rac{4}{3}aT^3V$ 。等温吸热

$$\Delta Q = T\Delta S = rac{4}{3}aT^3(V_2-V_1)$$

解:

在 T-S 图上讨论卡诺循环。等温膨胀吸热 $Q_1=T_1(S_2-S_1)$,等温压缩放出 $Q_2=T_2(S_2-S_1)$ 。故循环效率

$$\eta = 1 - rac{Q_2}{Q_1} = 1 - rac{T_2}{T_1}$$

4.19

2.18, 2.19, 2.20, 2.21, 2.22

2.18

解:

对于电介质,

$$dW = VEdD$$

介电常量 $\varepsilon(T) = D/E$,故

$$\left(\frac{\partial D}{\partial T}\right)_E = E \frac{\mathrm{d}\varepsilon}{\mathrm{d}T}, \ \left(\frac{\partial E}{\partial T}\right)_D = -\frac{D}{\varepsilon^2} \frac{\mathrm{d}\varepsilon}{\mathrm{d}T}$$

类比简单热力学系统,有

$$C_E - C_D = -VT \left(rac{\partial E}{\partial T}
ight)_D \left(rac{\partial D}{\partial T}
ight)_E = VTrac{DE}{arepsilon^2} \left(rac{\mathrm{d}arepsilon}{\mathrm{d}T}
ight)^2$$

2.19

证明:

对于磁介质,

$$dW = \mu_0 \mathcal{H} d\mathcal{M}$$

类比简单热力学系统,有

$$C_{\mathscr{H}}-C_{\mathscr{M}}=-\mu_0 T\left(rac{\partial \mathscr{H}}{\partial T}
ight)_{\mathscr{M}}\left(rac{\partial \mathscr{M}}{\partial T}
ight)_{\mathscr{H}}$$

$$=\mu_0 T \left(\frac{\partial \mathcal{H}}{\partial T}\right)_{\mathcal{M}}^2 \left(\frac{\partial \mathcal{M}}{\partial \mathcal{H}}\right)_T$$

解:

根据居里定律, $m = CV/T\mathcal{H}$,则

$$\left(\frac{\partial S}{\partial \mathscr{H}}\right)_T = \mu_0 \left(\frac{\partial m}{\partial T}\right)_{\mathscr{H}} = -\mu_0 \frac{CV}{T^2} \mathscr{H}$$

在等温过程中, 熵增

$$\Delta S = \int_0^H \left(\frac{\partial S}{\partial \mathscr{H}} \right)_T d\mathscr{H} = -\mu_0 \frac{CV}{2T^2} \mathscr{H}^2$$

故吸热

$$Q = T\Delta S = -\mu_0 rac{CV}{2T} \mathscr{H}^2$$

2.21

证明:

(a)

因为超导体有 $\mathcal{H}+\mathcal{M}=0$,故

$$\left(\frac{\partial \mathcal{M}}{\partial T}\right)_{\mathcal{H}} = \left(\frac{\partial \mathcal{H}}{\partial T}\right)_{\mathcal{M}} = 0$$

$$\left(\frac{\partial C_{\mathscr{M}}}{\partial \mathscr{M}}\right)_{T} = -\mu_{0}T \left(\frac{\partial^{2} \mathscr{H}}{\partial T^{2}}\right)_{\mathscr{M}} = 0$$

即 $C_{\mathscr{M}}$ 与 \mathscr{M} 无关,只是T的函数。

(b)

内能的全微分

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_{\mathscr{M}} \mathrm{d}T + \left(\frac{\partial U}{\partial \mathscr{M}}\right)_{T} \mathrm{d}\mathscr{M} = C_{\mathscr{M}} \mathrm{d}T - \mu_{0}\mathscr{M} \mathrm{d}\mathscr{M}$$

故

$$U = \int C_{\mathscr{M}} \mathrm{d}T - rac{\mu_0 \mathscr{M}^2}{2} + U_0$$

(c)

熵的全微分

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_{\mathscr{M}} \mathrm{d}T + \left(\frac{\partial S}{\partial \mathscr{M}}\right)_{T} \mathrm{d}\mathscr{M} = \frac{C_{\mathscr{M}}}{T} \mathrm{d}T$$

故

$$S = \int rac{C_{\mathscr{M}}}{T} \mathrm{d}T + S_0$$

2.22

解:

当 $dW = \mu_0 \mathcal{H} d\mathcal{M}$ 时,

$$\mathrm{d}F = -S\mathrm{d}T + \mu_0 \mathscr{H}\mathrm{d}\mathscr{M} = -S\mathrm{d}T + \mu_0 \frac{\mathscr{M}}{C/T}\mathrm{d}\mathscr{M}$$

积分得

$$F=rac{\mu_0\mathscr{M}^2}{2C/T}+F_0(T)$$

$$S = -\left(rac{\partial F}{\partial T}
ight)_{\mathscr{M}} = -rac{\mu_0\mathscr{M}^2}{2C} + S_0(T)$$

$$U = F + TS = U_0(T)$$

当 $dW = -\mu_0 \mathcal{M} d\mathcal{H}$ 时,

$$dF = -SdT - \mu_0 \mathcal{M}d\mathcal{H} = -SdT - \mu_0 C/T\mathcal{H}d\mathcal{H}$$

积分得

$$F=-rac{\mu_0 C/T\mathscr{H}^2}{2}+F_0(T)$$

$$S = -\left(rac{\partial F}{\partial T}
ight)_{\mathscr{M}} = -rac{\mu_0 C\mathscr{H}^2}{2T^2} + S_0(T)$$

$$U=F+TS=-\mu_0C/T\mathscr{H}^2+U_0(T)$$

两种表述的熵是等价的, 但是内能有所不同。后者描述的内能与磁场有关。

4.24

3.1, 3.2, 3.3, 3.4, 3.5, 4.11

3.1

证明:

(a)

在S,V不变的情况下,虚变动

$$\delta U < T\delta S - p\delta V = 0$$

故稳定平衡态的 U 最小。

(b)

在S,p不变的情况下,虚变动

$$\delta H < T\delta S + V\delta p = 0$$

故稳定平衡态的 H 最小。

(c)

在H,p不变的情况下,虚变动

$$\delta S > rac{1}{T}(\delta H - V \delta p) = 0$$

故稳定平衡态的 S 最大。

(d)

在F,V不变的情况下,虚变动

$$\delta T < rac{1}{S}(-\delta F - p\delta V) = 0$$

故稳定平衡态的 T 最小。

(e)

在G,p不变的情况下,虚变动

$$\delta T < rac{1}{S}(-\delta G + V\delta p) = 0$$

故稳定平衡态的 T 最小。

(f)

在U,S不变的情况下,虚变动

$$\delta V < rac{1}{p}(\delta U - T \delta S) = 0$$

故稳定平衡态的 V 最小。

(g)

在F,T不变的情况下,虚变动

$$\delta V < \frac{1}{p}(-\delta F - S\delta T) = 0$$

故稳定平衡态的 V 最小。

证明:

$$\delta^2 S = \left(rac{\partial^2 S}{\partial U^2}
ight) (\delta U)^2 + 2 \left(rac{\partial^2 S}{\partial V \partial U}
ight) (\delta U \delta V) + \left(rac{\partial^2 S}{\partial V^2}
ight) (\delta V)^2$$

由

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}, \ \left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T}$$

可得

$$\begin{split} \frac{\partial^2 S}{\partial U^2} &= \left(\frac{\partial (1/T)}{\partial U}\right)_V = -\frac{1}{T^2} \left(\frac{\partial T}{\partial U}\right)_V = \frac{1}{C_V T^2} \\ \frac{\partial^2 S}{\partial V \partial U} &= -\frac{1}{T^2} \left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{T^2} \frac{1}{C_V} \left[T \left(\frac{\partial p}{\partial T}\right)_V - p\right] = \frac{p}{C_V T} \left(\beta - \frac{1}{T}\right) \\ \frac{\partial^2 S}{\partial V^2} &= \left(\frac{\partial (p/T)}{\partial V}\right)_U = \frac{1}{T^2} \left[T \left(\frac{\partial p}{\partial V}\right)_U - p \left(\frac{\partial T}{\partial V}\right)_U\right] \\ &= -\frac{1}{T} \left[T \left(\frac{\partial p}{\partial T}\right)_V - p + C_V \left(\frac{\partial T}{\partial V}\right)_p\right] / \left[C_V \left(\frac{\partial T}{\partial p}\right)_V\right] + \frac{p}{T^2} \frac{1}{C_V} \left[T \left(\frac{\partial p}{\partial T}\right)_V - p\right] \\ &= -\frac{p^2 \beta^2}{C_V} + \frac{p^2 \beta}{C_V T} - \frac{1}{TV \kappa_T} + \frac{p^2}{T} \frac{\beta}{C_V} - \frac{p^2}{T^2} \frac{1}{C_V} \\ &= \frac{2p^2 \beta}{C_V T} - \frac{p^2}{C_V T^2} - \frac{p^2 \beta^2}{C_V} - \frac{1}{TV \kappa_T} \end{split}$$

即有所证式。

3.3

解:

对于孤立系统任意切分的两个子系统,有

$$\delta U_1 + \delta U_2 = 0, \ \delta V_1 + \delta V_2 = 0$$

系统熵变

$$\delta S = \delta S_1 + \delta S_2 = \delta U_1 \left(rac{1}{T_1} - rac{1}{T_2}
ight) + \delta V_1 \left(rac{p_1}{T_1} - rac{p_2}{T_2}
ight) = 0$$

故有 $p_1 = p_2 = p, T_1 = T_2 = T$ 。

稳定性要求 $\delta^2 S < 0$,故

$$\delta^2 S = \sum_{i=1,2} \left[-rac{C_{V,i}}{T^2} (\delta T)^2 + rac{1}{T} \left(rac{\partial p}{\partial V_i}
ight)_T (\delta V_i)^2
ight] < 0$$

故

$$C_{V,i}>0,\ \left(rac{\partial p}{\partial V_i}
ight)_T<0,\ i=1,2$$

3.4

证明:

$$C_p - C_V = T \left(rac{\partial p}{\partial T}
ight)_V \left(rac{\partial V}{\partial T}
ight)_p = -T \left(rac{\partial p}{\partial V}
ight)_T \left(rac{\partial V}{\partial T}
ight)_p^2 \geqslant 0$$

故

$$C_p\geqslant C_V>0$$

又

$$\left(rac{\partial p}{\partial V}
ight)_S/\left(rac{\partial p}{\partial V}
ight)_T=\left(rac{\partial S}{\partial T}
ight)_V/\left(rac{\partial S}{\partial T}
ight)_p=C_p/C_V\geqslant 1$$

故

$$\left(\frac{\partial p}{\partial V}\right)_S \geqslant \left(\frac{\partial p}{\partial V}\right)_T < 0$$

3.5

解:

两个子系统间有 $p_1 = p_2 = p, T_1 = T_2 = T$ 。

根据

$$T\delta S_i = \delta U_i + p\delta V_i$$

变分得

$$\delta T \delta S_i + T \delta^2 S_i = \delta^2 U_i + \delta p \delta V_i + p \delta^2 V_i$$

对i求和,注意到U,V是不变量,有

$$\delta^2 S = \sum_{i=1,2} rac{\delta p \delta V_i - \delta T \delta S_i}{T} < 0$$

根据两系统独立性,有

$$\delta p_i \delta V_i - \delta T_i \delta S_i < 0, \ i = 1, 2$$

取T,V为自变量,有

$$C_{V,i}>0,\, \left(rac{\partial V_i}{\partial p}
ight)_T<0$$

取S, p为自变量,有

$$C_{p,i}>0,\, \left(rac{\partial V_i}{\partial p}
ight)_S<0$$

4.11

证明:

表面系统中, $dW = \sigma \mathrm{d}A$ 。根据自由能 $F = -S\mathrm{d}T + \sigma \mathrm{d}A$ 的全微分

$$\left(\frac{\partial \sigma}{\partial T}\right)_A = \left(\frac{\partial S}{\partial A}\right)_T$$

根据热力学第三定律,

$$\lim_{T o 0^+} \left(rac{\partial S}{\partial A}
ight)_T = 0$$

又 $\sigma = \sigma(T)$, 与 A 无关, 故

$$\lim_{T o 0^+}rac{\mathrm{d}\sigma}{\mathrm{d}T}=\lim_{T o 0^+}\left(rac{\partial S}{\partial A}
ight)_T=0$$

4.26

3.6, 3.7, 3.8, 3.10, 3.11, 3.13

3.6

证明:

(a)

自由能的全微分

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}n$$

得

$$\left(\frac{\partial \mu}{\partial T}\right)_{V,n} = -\left(\frac{\partial S}{\partial n}\right)_{V,T}$$

(b)

吉布斯自由能的全微分

$$dG = -SdT + Vdp + \mu dn$$

得

$$\left(\frac{\partial \mu}{\partial p}\right)_{T,n} = -\left(\frac{\partial V}{\partial n}\right)_{T,n}$$

3.7

证明:

自由能的全微分

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}n$$

得

$$\mu = \left(\frac{\partial F}{\partial n}\right)_{V,T}, \ \left(\frac{\partial \mu}{\partial T}\right)_{V,n} = -\left(\frac{\partial S}{\partial n}\right)_{V,T}$$

又F = U - TS,得

$$\left(\frac{\partial F}{\partial n}\right)_{V,T} = \left(\frac{\partial U}{\partial n}\right)_{V,T} - T\left(\frac{\partial S}{\partial n}\right)_{V,T}$$

故

$$\left(\frac{\partial U}{\partial n}\right)_{V,T} - \mu = -T \left(\frac{\partial \mu}{\partial T}\right)_{V,n}$$

3.8

解:

由一阶变分

$$\delta S^i = rac{\delta U^i + p^i \delta V^i - \mu^i \delta n^i}{T^i}$$

得到
$$p^1=p^2=p, T^1=T^2=T, \mu^1=\mu^2=\mu$$
。二阶变分
$$\delta^2S^i=\frac{\delta^2U^i+p\delta^2V^i+\delta p\delta V^i-\mu\delta^2n^i-\delta\mu\delta n^i-\delta T\delta S^i}{T}$$

对i求和,注意到U,V,n是不变量,有

$$\delta^2 S = \sum_{i=1,2} rac{\delta p \delta V^i - \delta \mu \delta n^i - \delta T \delta S^i}{T} < 0$$

根据两系统独立性,有

$$\delta p^i \delta V^i - \delta T^i \delta S^i < 0, \; i=1,2$$

取T,V为自变量,有

$$C_V^i>0,\, \left(rac{\partial V^i}{\partial p}
ight)_T<0$$

取 S, p 为自变量,有

$$C_p^i > 0, \, \left(rac{\partial V^i}{\partial p}
ight)_S < 0$$

3.10

证明:

相变潜热即焓变 $\Delta H_m = L$ 。根据克拉伯龙方程,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T\Delta V_m} \Rightarrow \Delta V_m = \frac{L}{T}\frac{\mathrm{d}T}{\mathrm{d}p}$$

故内能变化

$$\Delta U_m = \Delta H_m - p \Delta V_m = L \left(1 - rac{p}{T} rac{\mathrm{d}T}{\mathrm{d}p}
ight)$$

若一相为理想气体,另一相为凝聚态,则

$$\Delta V_m = V_{g,m} = rac{RT}{p}$$

那么

$$\Delta U_m = L - RT$$

3.11

解:

联立两蒸气压方程, 得到

$$\ln p_0 = 27.92 - rac{3754}{T_0} = 24.38 - rac{3063}{T_0} \Rightarrow T_0 = 195.2\,\mathrm{K}$$

根据蒸气压近似方程,

$$\ln p = -\frac{L}{RT} + A$$

得到

$$L$$
汽 = $3754 \times 8.31 = 3.12 \times 10^4 \,\mathrm{J}$
 $L_{\mathcal{H}} = 3063 \times 8.31 = 2.55 \times 10^4 \,\mathrm{J}$

3.13

证明:

相变潜热 $L_m=H_m^{eta}-H_m^{lpha}$,故

$$\begin{split} \frac{\mathrm{d}L}{\mathrm{d}T} &= \left(\frac{\partial H_m^\beta}{\partial T}\right)_p + \left(\frac{\partial H_m^\beta}{\partial p}\right)_T \frac{\mathrm{d}p}{\mathrm{d}T} - \left(\frac{\partial H_m^\alpha}{\partial T}\right)_p - \left(\frac{\partial H_m^\beta}{\partial p}\right)_T \frac{\mathrm{d}p}{\mathrm{d}T} \\ &= C_p^\beta - C_p^\alpha + (V_m^\beta - V_m^\alpha) \frac{\mathrm{d}p}{\mathrm{d}T} - T \left[\left(\frac{\partial V_m^\beta}{\partial T}\right)_p - \left(\frac{\partial V_m^\alpha}{\partial T}\right)_p \right] \frac{\mathrm{d}p}{\mathrm{d}T} \\ &= C_p^\beta - C_p^\alpha + \frac{L}{T} - \left[\left(\frac{\partial V_m^\beta}{\partial T}\right)_p - \left(\frac{\partial V_m^\alpha}{\partial T}\right)_p \right] \frac{L}{V_m^\beta - V_m^\alpha} \end{split}$$

若 eta 相是气相,lpha 相是凝聚相,则 V_m^lpha 项可忽略。故

$$rac{\mathrm{d}L}{\mathrm{d}T} = C_p^eta - C_p^lpha + rac{L}{T} - \left(rac{\partial V_m^eta}{\partial T}
ight)_p rac{L}{V_m^eta} = C_p^eta - C_p^lpha$$

4.27

3.14, 3.15, 3.16, 3.19, 3.20, 3.21, 4.3, 4.8, 4.13

3.14

证明:

由

$$\frac{\mathrm{d}L}{\mathrm{d}T} = C_p^{\beta} - C_p^{\alpha}$$

积分得

$$L = (C_p^{\beta} - C_p^{\alpha})T + L_0$$

又

$$rac{1}{p}rac{\mathrm{d}p}{\mathrm{d}T} = rac{L}{RT^2} = rac{L_0}{RT^2} + rac{C_p^eta - C_p^lpha}{RT}$$

积分得

$$\ln p = A - \frac{B}{T} + C \ln T$$

其中 $B=L_0/R, C=(C_p^{eta}-C_p^{lpha})/R$ 。

3.15

证明:

根据克拉伯龙方程,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{pL}{RT^2}$$

对理想气体,有

$$\left(rac{\partial V_m}{\partial T}
ight)_p = rac{1}{T}, \; \left(rac{\partial V_m}{\partial p}
ight)_T = -rac{1}{p},$$

故

$$egin{aligned} rac{1}{V_m}rac{\mathrm{d}V_m}{\mathrm{d}T} &= rac{1}{V_m}\left[\left(rac{\partial V_m}{\partial T}
ight)_p + \left(rac{\partial V_m}{\partial p}
ight)_Trac{\mathrm{d}p}{\mathrm{d}T}
ight] \ &= rac{1}{T} - rac{L}{RT^2} \end{aligned}$$

证明:

范式气体方程

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

等温线极值点

$$\left(rac{\partial p}{\partial V_m}
ight)_T = -rac{RT}{(V_m-b)^2} + rac{2a}{V_m^3} = 0$$

故有

$$pV_m^3 = \left(rac{RT}{V_m - b} - rac{a}{V_m^2}
ight)V_m^3 = \left(rac{2a}{V_m^3}(V_m - b) - rac{a}{V_m^2}
ight)V_m^3 = a(V_m - 2b)$$

区域 Ⅱ 为不稳定平衡点,会迅速演化到两相平衡的稳定状态。区域 Ⅰ,Ⅲ 为亚稳态,可以作为过热液体和过饱和蒸汽单相存在。

3.19

证明:

二级相变下,有 $\mathrm{d}v^1=\mathrm{d}v^2,\mathrm{d}s^1=\mathrm{d}s^2$ 。由

$$\mathrm{d}v = \left(rac{\partial v}{\partial p}
ight)_T \mathrm{d}p + \left(rac{\partial v}{\partial T}
ight)_p \mathrm{d}T = -\kappa v \mathrm{d}p + \alpha v \mathrm{d}T$$
 $\mathrm{d}s = \left(rac{\partial s}{\partial p}
ight)_T \mathrm{d}p + \left(rac{\partial s}{\partial T}
ight)_p \mathrm{d}T = -\alpha v \mathrm{d}p + rac{C_p}{T} \mathrm{d}T$

故

$$-\kappa^1\mathrm{d}p + lpha^1\mathrm{d}T = -\kappa^2\mathrm{d}p + lpha^2\mathrm{d}T \ -lpha^1v\mathrm{d}p + rac{C_p^1}{T}\mathrm{d}T = -lpha^2v\mathrm{d}p + rac{C_p^2}{T}\mathrm{d}T$$

整理得到

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\alpha^2 - \alpha^1}{\kappa^2 - \kappa^1} = \frac{C_p^2 - C_p^1}{Tv(\alpha^2 - \alpha^1)}$$

证明:

平衡下自由能取极小值,有

$$F = F_0, \; T > T_C; \quad F = F_0 - rac{a^2}{4b}, \; T < T_C$$

故熵

$$S=-\left(rac{\partial F}{\partial T}
ight)_V=-F_0'(T),\; T>T_C \ S=-\left(rac{\partial F}{\partial T}
ight)_V=-F_0'(T)+rac{a(T)a'(T)}{2b}=-F_0'(T)+rac{a_0^2}{2b}rac{T-T_C}{T_C^2},\; T< T_C$$

在 $T = T_C$ 处,熵连续。

3.21

解:

根据朗道自由能,得到

$$\mu_0 \mathscr{H} = a\mathscr{M} + b\mathscr{M}^3$$

求导得

$$\left(\frac{\partial \mathcal{H}}{\partial T}\right)_{\mathcal{M}} = \frac{a_0}{\mu_0 T_C} \mathcal{M}$$

故

$$C_{\mathscr{H}}-C_{\mathscr{M}}=\mu_{0}T\left(rac{\partial\mathscr{H}}{\partial T}
ight)_{\mathscr{M}}^{2}\left(rac{\partial\mathscr{M}}{\partial\mathscr{H}}
ight)_{T}=Trac{a_{0}^{2}\mathscr{M}^{2}}{\mu_{0}T_{C}^{2}}\left(rac{\partial\mathscr{M}}{\partial\mathscr{H}}
ight)_{T}$$

因为无序相 $\mathscr{M}=0$,故 $C_{\mathscr{H}}-C_{\mathscr{M}}=0$ 。对于有序相,

$$egin{align} \mathscr{M}^2 &= -rac{a_0}{b}t \ \left(rac{\partial \mathscr{M}}{\partial \mathscr{H}}
ight)_T &= -rac{\mu_0}{2a_0}rac{1}{t} \end{aligned}$$

故

$$C_{\mathscr{H}}-C_{\mathscr{M}}=rac{a_0^2T}{2bT_C^2}$$

4.3

证明:

(a)

混合前 $G_0=n_1g_1+n_2g_2$,混合后 $G=n_1\mu_1+n_2\mu_2$ 。故

$$\Delta G = G - G_0 = n_1 RT \ln x_1 + n_2 RT \ln x_2$$

(b)

$$\Delta V = \left(\frac{\partial \Delta G}{\partial p}\right)_{T.n.} = 0$$

(c)

$$\Delta S = -\left(rac{\partial \Delta G}{\partial T}
ight)_{n\,n_i} = -R(n_1 \ln x_1 + n_2 \ln x_2)$$

(d)

等温等压下, 焓变

$$\Delta H = \Delta G + T\Delta S = 0$$

(e)

$$\Delta U = \Delta H - p\Delta V = 0$$

4.8

解:

(a)

混合前

$$p_1V_1 = n_1RT, \ p_2V_2 = n_2RT$$

混合后

$$p(V_1 + V_2) = (n_1 + n_2)RT$$

故

$$p=rac{n_1+n_2}{n_1/p_1+n_2/p_2}$$

(b)

$$\Delta S = \Delta S_1 + \Delta S_2 = n_1 R \ln rac{V_1 + V_2}{V_1} + n_2 R \ln rac{V_1 + V_2}{V_2}$$

(c)

$$\Delta S = (n_1 + n_2) R \ln rac{V_1 + V_2}{n_1 + n_2} - n_1 R \ln rac{V_1}{n_1} - n_2 R \ln rac{V_2}{n_2}$$

4.13

解:

温度为 T_0 的白锡的熵

$$S(T_0) = S_w(0) + \int_0^{T_0} rac{C_w(T)}{T} \, \mathrm{d}T = S_g(0) + \int_0^{T_0} rac{C_g(T)}{T} \, \mathrm{d}T + rac{L}{T_0}$$

故

$$egin{align} S_w(0) - S_g(0) &= \int_0^{T_0} rac{C_g(T)}{T} \, \mathrm{d}T - \int_0^{T_0} rac{C_w(T)}{T} \, \mathrm{d}T + rac{L}{T_0} \ &= 44.12 - 51.44 + rac{2242}{292} = 0.25 \, \mathrm{J/mol.K} \ \end{split}$$

是适用的

5.10

6.1, 6.2, 6.3, 6.4

证明:

在体积 $V=L^3$ 内,自由粒子的量子态数目有

$$\mathrm{d}n = \frac{V}{h^3} \mathrm{d}^3 p = \frac{4\pi V}{h^3} p^2 \mathrm{d}p$$

根据自由粒子能量动量关系,有

$$arepsilon=rac{p^2}{2m}$$

故

$$\mathrm{d}n = D(\varepsilon)\mathrm{d}\varepsilon = rac{4\pi V}{h^3}p^2rac{\mathrm{d}p}{\mathrm{d}\varepsilon}\mathrm{d}\varepsilon = rac{2\pi V}{h^3}(2m)^{3/2}arepsilon^{1/2}\mathrm{d}arepsilon$$

6.2

证明:

在长度 L 内,自由粒子可能的状态数为

$$\mathrm{d}n = \frac{2L}{h}\mathrm{d}p$$

根据 $arepsilon=p^2/2m$,得

$$\mathrm{d}n = D(\varepsilon)\mathrm{d}\varepsilon = \frac{2L}{h}\frac{\mathrm{d}p}{\mathrm{d}\varepsilon}\mathrm{d}\varepsilon = \frac{2L}{h}\sqrt{\frac{m}{2\varepsilon}}\mathrm{d}\varepsilon$$

6.3

证明:

在面积 L^2 内,自由粒子可能的状态数为

$$\mathrm{d}n = \frac{2\pi L^2}{h^2} p \mathrm{d}p$$

根据 $arepsilon=p^2/2m$,得

$$\mathrm{d}n = D(\varepsilon)\mathrm{d}\varepsilon = rac{2\pi L^2}{h^2}prac{\mathrm{d}p}{\mathrm{d}\varepsilon}\mathrm{d}\varepsilon = rac{2\pi L^2}{h^2}m\mathrm{d}\varepsilon$$

解:

在体积 $V=L^3$ 内,相对论粒子的量子态数目有

$$\mathrm{d}n = \frac{4\pi V}{h^3} p^2 \mathrm{d}p$$

根据极端相对论粒子能量动量关系 $\varepsilon=cp$,有

$$\mathrm{d}n = D(\varepsilon)\mathrm{d}\varepsilon = \frac{4\pi V}{h^3}p^2\frac{\mathrm{d}p}{\mathrm{d}\varepsilon}\mathrm{d}\varepsilon = \frac{4\pi V}{c^3h^3}\varepsilon^2\mathrm{d}\varepsilon$$

5.22

6.5

6.5

证明:

两种粒子的分布 $\{a_l\}$, $\{a'_l\}$ 满足

$$\sum_{l}a_{l}=N,\;\sum_{l}a_{l}'=N',\;\sum_{l}(a_{l}arepsilon_{l}+a_{l}'arepsilon_{l}')=E$$

由于粒子可分辨,处在一个个体量子态的粒子数不受限制,故微观状态数有

$$egin{aligned} \Omega &= rac{N!}{\prod_l a_l!} \prod_l \omega_l^{a_l} \ \Omega' &= rac{N'!}{\prod_l a_l'!} \prod_l \omega_l'^{a_l'} \end{aligned}$$

系统的总状态数 $\Omega\Omega'$ 应该达到极大值。故

$$\ln(\Omega\Omega') = N \ln N - \sum_l a_l \ln a_l + \sum_l a_l \ln \omega_l + N' \ln N' - \sum_l a_l' \ln a_l' + \sum_l a_l' \ln \omega_l'$$

取极大值。对分布取变分得

$$\delta \ln(\Omega \Omega') = -\sum_l \ln rac{a_l}{\omega_l} \delta a_l - \sum_l \ln rac{a_l'}{\omega_l'} \delta a_l' = 0$$

由约束条件,

$$\delta N = \sum_l \delta a_l = 0, \; \delta N' = \sum_l \delta a_l' = 0, \; \delta E = \sum_l (arepsilon_l \delta a_l + arepsilon_l' \delta a_l') = 0$$

对任意 α, α', β 有

$$\delta \ln(\Omega\Omega') - lpha \delta N - lpha' \delta N' - eta \delta E \ = -\sum_{l} \left(\ln rac{a_{l}}{\omega_{l}} + lpha + eta arepsilon
ight) \delta a_{l} - \sum_{l} \left(\ln rac{a'_{l}}{\omega'_{l}} + lpha' + eta arepsilon'
ight) \delta a'_{l} = 0$$

故

$$\ln rac{a_l}{\omega_l} + lpha + eta arepsilon = \ln rac{a_l'}{\omega_l'} + lpha' + eta arepsilon' = 0$$

即分布满足

$$a_l = \omega_l \mathrm{e}^{-lpha - eta arepsilon_l}, \; a_l' = \omega_l' \mathrm{e}^{-lpha' - eta arepsilon_l'}$$

系数由约束式确定。故互为热平衡的两个子系统有相同的 eta。

5.24

6.6

6.6

证明:

由上题我们知道,两种不同的粒子相互不影响,最后的状态数是对两种分布变分之和,不同粒子的区别只是状态数的表达式不同。故我们可以分开讨论,详细过程与上题相同。

若粒子为波色子,则微观状态数

$$\Omega_B = \prod_l rac{(\omega_l + a_l - 1)!}{a_l!(\omega_l - 1)!}$$

若粒子为费米子,则微观状态数

$$\Omega_F = \prod_l rac{\omega_l!}{a_l!(\omega_l - a_l)!}$$

故

$$\delta \ln \Omega_B = \sum_l \ln rac{\omega_l + a_l}{a_l} \delta a_l, \; \delta \ln \Omega_F = \sum_l \ln rac{\omega_l - a_l}{a_l} \delta a_l$$

以下步骤相同。两种粒子的分布 $\{a_l\},\{a_l'\}$ 满足

$$\sum_{l}a_{l}=N,\;\sum_{l}a_{l}'=N',\;\sum_{l}(a_{l}arepsilon_{l}+a_{l}'arepsilon_{l}')=E$$

系统的总状态数 $\Omega\Omega'$ 应该达到极大值。对分布取变分,两者求和为0。由约束条件,

$$\delta N = \sum_l \delta a_l = 0, \; \delta N' = \sum_l \delta a_l' = 0, \; \delta E = \sum_l (arepsilon_l \delta a_l + arepsilon_l' \delta a_l') = 0$$

对任意 α, α', β 有

$$\delta \ln(\Omega \Omega') - \alpha \delta N - \alpha' \delta N' - \beta \delta E = 0$$

故对于波色子,有

$$\ln rac{\omega_l + a_l}{a_l} - lpha - eta arepsilon_l = 0$$

故对于费米子,有

$$\ln rac{\omega_l - a_l}{a_l} - lpha - eta arepsilon_l = 0$$

即波色子和费米子的分布分别满足

$$a_{l,B} = rac{\omega_l}{\exp(lpha + eta arepsilon_l) - 1}, \; a_{l,F} = rac{\omega_l}{\exp(lpha + eta arepsilon_l) + 1}$$

系数由约束式确定。

5.29

7.1, 7.2, 7.3, 7.4, 7.5, 7.6

7.1

证明:

取 L^3 的立方体,对于非相对论的粒子

$$arepsilon arepsilon = rac{p^2}{2m} = rac{1}{2m} \left(rac{2\pi\hbar}{L}
ight)^2 (n_x^2 + n_y^2 + n_z^2), \quad n_x, n_y, n_z \in \mathbb{Z}$$

我们记

$$l=n_{x}^{2}+n_{y}^{2}+n_{z}^{2},\;a_{l}=rac{(2\pi\hbar)^{2}}{2m}l$$

故 $arepsilon_l = a_l V^{-2/3}$ 。根据公式,

$$p=-\sum_{l}a_{l}rac{\partialarepsilon_{l}}{\partial V}=-\sum_{l}a_{l}\cdot-rac{2}{3}a_{l}V^{-5/3}=\sum_{l}rac{2}{3V}a_{l}arepsilon_{l}=rac{2}{3}rac{U}{V}$$

与具体分布无关,故均适用。

7.2

证明:

取 L^3 的立方体,对于极端相对论的粒子

$$arepsilon=cp=crac{2\pi\hbar}{L}(n_x^2+n_y^2+n_z^2)^{1/2},\quad n_x,n_y,n_z\in\mathbb{Z}$$

我们记

$$l=(n_x^2+n_y^2+n_z^2)^{1/2},\; a_l=2\pi c\hbar l$$

故 $\varepsilon_l = a_l V^{-1/3}$ 。根据公式,

$$p = -\sum_l a_l rac{\partial arepsilon_l}{\partial V} = -\sum_l a_l \cdot -rac{1}{3} a_l V^{-4/3} = \sum_l rac{1}{3V} a_l arepsilon_l = rac{1}{3} rac{U}{V}$$

与具体分布无关, 故均适用。

7.3

证明:

不同能量零点的选取,有 $arepsilon_l^* = arepsilon_l + \Delta$ 。故配分函数

$$Z_1 = \sum_l \omega_l \mathrm{e}^{-eta arepsilon_l}$$

$$Z_1^* = \sum_l \omega_l \mathrm{e}^{-eta arepsilon_l^*} = \mathrm{e}^{-eta \Delta} \sum_l \omega_l \mathrm{e}^{-eta arepsilon_l} = \mathrm{e}^{-eta \Delta} Z_1$$

这样两个配分函数之差 $\ln Z_1^* = \ln Z_1 - eta \Delta$ 。故相应热力学函数有

$$U^* = -Nrac{\partial}{\partialeta}\ln Z_1^* = U + N\Delta$$
 $p^* = rac{N}{eta}rac{\partial}{\partial V}\ln Z_1^* = p$ $S^* = Nk\left(\ln Z_1^* - etarac{\partial}{\partialeta}\ln Z_1^*
ight) = S$

7.4

证明:

粒子处在量子态 s 上的概率

$$P_s = rac{\mathrm{e}^{-eta arepsilon_s}}{Z_1}$$

取对数得

$$\ln P_s = -\ln Z_1 - \beta \varepsilon_s$$

系统的熵为

$$egin{aligned} S &= Nk \left(\ln Z_1 - eta rac{\partial}{\partial eta} \ln Z_1
ight) = Nk (\ln Z_1 + eta ar{arepsilon}) \ &= Nk (\ln Z_1 + eta \sum_s P_s arepsilon_s) \ &= Nk \sum_s P_s (\ln Z_1 + eta arepsilon_s) \ &= -Nk \sum_s P_s \ln P_s \end{aligned}$$

对于满足经典极限的非定域系统, 熵

$$egin{aligned} S &= Nk \left(\ln Z_1 - eta rac{\partial}{\partial eta} \ln Z_1
ight) - k \ln N! \ &= -Nk \sum_s P_s \ln P_s - Nk (\ln N - 1) \ &= -k \sum_s f_s \ln f_s + Nk \end{aligned}$$

7.5

证明:

所有随机分布的微观状态数为

$$\Omega = \frac{N!}{(Nx)![N(1-x)]!}$$

故熵

$$S = k \ln \Omega = k \ln rac{N!}{(Nx)![N(1-x)]!} \ = k \{ N(\ln N - 1) - Nx(\ln Nx - 1) - N(1-x)[\ln N(1-x) - 1] \} \ = -Nk[x \ln x + (1-x) \ln(1-x)]$$

证明:

(a)

格点和间隙的位置都是 N 选 n,故可能的微观状态数为

$$\Omega = \left(rac{N!}{n!(N-n)!}
ight)^2$$

故熵

$$S = k \ln \Omega = 2k \ln rac{N!}{n!(N-n)!}$$

(b)

自由能

$$F=nu-TS=nu-2kT\lnrac{N!}{n!(N-n)!} \ =nu-2kT[N\ln N-n\ln n-(N-n)\ln(N-n)]$$

自由能极小条件

$$\frac{\partial F}{\partial n} = u - 2kT \ln \frac{N-n}{n} \approx u - 2kT \ln \frac{N}{n} = 0 \quad (n \ll N)$$

得到

$$npprox N\mathrm{e}^{-rac{u}{2kT}}$$

5.31

7.7, 7.8, 7.9, 7.11, 7.14, 7.16

7.7

证明:

可能的微观状态数为

$$\Omega = \frac{N!}{n!(N-n)!}$$

故熵

$$S = k \ln \Omega = k \ln rac{N!}{n!(N-n)!}$$

自由能

$$F = nW - TS = nW - kT \ln \frac{N!}{n!(N-n)!}$$

= $nW - kT[N \ln N - n \ln n - (N-n) \ln(N-n)]$

自由能极小条件

$$rac{\partial F}{\partial n} = W - kT \ln rac{N-n}{n} pprox W - kT \ln rac{N}{n} = 0 \quad (n \ll N)$$

得到

$$npprox N\mathrm{e}^{-rac{W}{kT}}$$

7.8

解:

探测器只能探测沿着一个方向传播的光的频率。根据对称性,我们不妨设探测器检测的光来自 z 方向。根据多普勒效应,频率改变

$$\Delta \omega = \omega - \omega_0 = \omega_0 rac{v_z}{c} \quad (v_z \ll c)$$

故频率分布即为速度分布。 根据速度分布律,

$$f_v(v_z)\mathrm{d}v_z=\mathrm{e}^{-rac{m}{2kT}v_z^2}\mathrm{d}v_z$$

故有频率分布

$$f_{\omega}(\omega)\mathrm{d}\omega=rac{c}{\omega_{0}}\mathrm{e}^{-rac{m}{2kT}rac{(\omega-\omega_{0})^{2}}{(\omega_{0}/c)^{2}}}\mathrm{d}\omega$$

证明:

以气体本身为参考系,相对实验室系以恒定速度沿着z方向运动。在气体参考系即零动量系中,气体自 然满足玻尔兹曼分布,即

$$f=\mathrm{e}^{-lpha-rac{eta}{2m}(p_x^2+p_y^2+p_z^2)}rac{V\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z}{\hbar^3}$$

换回实验室系后, 动量发生平移, 即

$$f'=\mathrm{e}^{-lpha-rac{eta}{2m}[p_x^2+p_y^2+(p_z-p_0)^2]}rac{V\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z}{\hbar^3}$$

7.11

解:

二维气体的速度分布为

$$f_{ec{v}}(ec{v}) = rac{m}{2\pi kT} \mathrm{e}^{-rac{m}{2kT}(v_x^2 + v_y^2)} \mathrm{d}v_x \mathrm{d}v_y$$

速率分布为

$$f(v) = rac{m}{2\pi kT} \mathrm{e}^{-rac{m}{2kT}v^2} 2\pi v \mathrm{d}v = rac{m}{kT} \mathrm{e}^{-rac{m}{2kT}v^2} v \mathrm{d}v$$

故平均速率, 最概然速率, 方均根速率分别为

$$ar{v} = \int v f(v) \mathrm{d}v = rac{m}{kT} \int_0^{+\infty} \mathrm{e}^{-rac{m}{2kT}v^2} v^2 \mathrm{d}v = \sqrt{rac{\pi kT}{2m}} \ rac{\mathrm{d}f(v)}{\mathrm{d}v} = 0 \Rightarrow v_m = \sqrt{rac{kT}{m}} \ v_s = \sqrt{ar{v}^2} = \sqrt{\int v^2 f(v) \mathrm{d}v} = \sqrt{rac{m}{kT}} \int_0^{+\infty} \mathrm{e}^{-rac{m}{2kT}v^2} v^3 \mathrm{d}v = \sqrt{rac{2kT}{m}} \ v_s = \sqrt{rac{m}{kT}} \int_0^{+\infty} \mathrm{e}^{-rac{m}{2kT}v^2} v^3 \mathrm{d}v = \sqrt{rac{2kT}{m}} \ v_s = \sqrt{rac{m}{kT}} \int_0^{+\infty} \mathrm{e}^{-rac{m}{2kT}v^2} v^3 \mathrm{d}v = \sqrt{rac{2kT}{m}} \ v_s = \sqrt{rac{m}{kT}} \int_0^{+\infty} \mathrm{e}^{-rac{m}{2kT}v^2} v^3 \mathrm{d}v = \sqrt{rac{m}{m}} \ v_s = \sqrt{n} \ v_s = \sqrt{n}$$

解:

泻流分布

$$\mathrm{d}\Gamma(v) = \pi n \left(rac{m}{2\pi kT}
ight)^{3/2} \mathrm{e}^{-rac{m}{2kT}v^2} v^3 \mathrm{d}v$$

故平均速率, 方均根速率, 平均能量分别为

$$ar{v} = rac{\int v \mathrm{d}\Gamma(v)}{\int \mathrm{d}\Gamma(v)} = rac{\int_0^{+\infty} \mathrm{e}^{-rac{m}{2kT}v^2} v^4 \mathrm{d}v}{\int_0^{+\infty} \mathrm{e}^{-rac{m}{2kT}v^2} v^3 \mathrm{d}v} = \sqrt{rac{9\pi kT}{8m}}$$

$$v_s = \sqrt{ar{v^2}} = \sqrt{rac{\int v^2 \mathrm{d}\Gamma(v)}{\int \mathrm{d}\Gamma(v)}} = \sqrt{rac{\int_0^{+\infty} \mathrm{e}^{-rac{m}{2kT}v^2}v^5 \mathrm{d}v}{\int_0^{+\infty} \mathrm{e}^{-rac{m}{2kT}v^2}v^3 \mathrm{d}v}} = \sqrt{rac{4kT}{m}}$$

$$ar{E_k}=rac{1}{2}mar{v^2}=2kT$$

7.16

解:

$$arepsilon arepsilon = rac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + ax^2 + bx = rac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + a\left(x + rac{b}{2a}
ight)^2 - rac{b^2}{4a}$$

根据能量均分定理,

$$ar{arepsilon} = rac{1}{2m}(ar{p_x^2} + ar{p_y^2} + ar{p_z^2}) + aigg(x + rac{b}{2a}igg)^2 - rac{b^2}{4a} = 2kT - rac{b^2}{4a}$$

6.5

7.10, 7.12, 7.13

解:

速度分布满足

$$f=\left(rac{m}{2\pi kT}
ight)^{3/2}\mathrm{e}^{-rac{m}{2kT}[v_x^2+v_y^2+(v_z-v_0)^2]}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$$

故平均平动动能

$$egin{aligned} ar{arepsilon} &= \left(rac{m}{2\pi kT}
ight)^{3/2} \iiint rac{1}{2} m(v_x^2 + v_y^2 + v_z^2) \mathrm{e}^{-rac{m}{2kT}[v_x^2 + v_y^2 + (v_z - v_0)^2]} \mathrm{d}v_x \mathrm{d}v_y \mathrm{d}v_z \ &= kT + \left(rac{m}{2\pi kT}
ight)^{1/2} \int_{-\infty}^{+\infty} rac{1}{2} m v_z^2 \mathrm{e}^{-rac{m}{2kT}(v_z - v_0)^2} \mathrm{d}v_z \ &= kT + rac{1}{2} kT + m v_0^2 - rac{1}{2} m v_0^2 = rac{3}{2} kT + rac{1}{2} m v_0^2 \end{aligned}$$

7.12

解:

两个粒子的速度联合分布

$$\left(rac{m}{2\pi kT}
ight)^{3/2} {
m e}^{-rac{mec{v}_1^2}{2kT}} {
m d}ec{v}_1 \left(rac{m}{2\pi kT}
ight)^{3/2} {
m e}^{-rac{mec{v}_2^2}{2kT}} {
m d}ec{v}_2$$

做变换

$$ec{v}_c = rac{1}{2}(ec{v}_1 + ec{v}_2), \; ec{v}_r = ec{v}_1 - ec{v}_2$$

又因为

$$rac{1}{2}mec{v}_{1}^{2}+rac{1}{2}mec{v}_{2}^{2}=rac{1}{2}2mec{v}_{c}^{2}+rac{1}{2}rac{m}{2}ec{v}_{r}^{2}$$

故联合分布可以写为

$$\left(rac{2m}{2\pi kT}
ight)^{3/2} {
m e}^{-rac{2mec{v}_c^2}{2kT}} {
m d}ec{v}_c \left(rac{m/2}{2\pi kT}
ight)^{3/2} {
m e}^{-rac{mec{v}_r^2/2}{2kT}} {
m d}ec{v}_r$$

其中可以看出第二项为相对速度分布。积分得相对速率分布

$$4\pi \left(rac{m/2}{2\pi kT}
ight)^{3/2} \mathrm{e}^{-rac{mv_r^2/2}{2kT}} v_r^2 \mathrm{d}v_r$$

平均相对速率

$$ar{v}_r = 4\pi \int_0^{+\infty} \left(rac{m/2}{2\pi kT}
ight)^{3/2} {
m e}^{-rac{mv_r^2/2}{2kT}} v_r^3 {
m d} v_r = \sqrt{rac{8kT}{\pi m/2}} = \sqrt{2}ar{v}$$

7.13

证明:

单位速度分布,单位时间碰壁(假设为z方向垂直)的分子数为

$$d\Gamma = f(\vec{v})v_z d\vec{v} = f(\vec{v})v\cos\theta v^2\sin\theta dv d\theta d\phi$$

角向积分得

$$\int_0^{2\pi} \int_0^{\pi/2} \cos \theta \sin \theta \mathrm{d} \theta \mathrm{d} \phi = \pi$$

故得泻流分布

$$\mathrm{d}\Gamma(v) = \pi n \left(rac{m}{2\pi kT}
ight)^{3/2} \mathrm{e}^{-rac{mv^2}{2kT}} v^3 \mathrm{d}v$$

6.7

7.17, 7.18, 7.19, 7.20, 7.21, 7.22, 7.23, 7.24

7.17

证明:

重力场下, 粒子能量为

$$arepsilon = rac{1}{2m}(p_x^2+p_y^2+p_z^2)+mgz$$

故配分函数

- - - - -

$$egin{aligned} Z_1 &= rac{1}{h^3} \iiint \iint \int \mathrm{e}^{-rac{eta}{2m}(p_x^2 + p_y^2 + p_z^2) - eta m g z} \, \mathrm{d}^3 x \mathrm{d}^3 p \ &= \left(rac{2\pi m}{h^2 eta}
ight)^{3/2} \iint \mathrm{d} x \mathrm{d} y \int_0^H \mathrm{e}^{-eta m g z} \, \mathrm{d} z \ &= \left(rac{2\pi m}{h^2 eta}
ight)^{3/2} S rac{1 - \mathrm{e}^{-eta m g H}}{eta m g} \end{aligned}$$

气体内能

$$U=-Nrac{\partial}{\partialeta}\ln Z_1=rac{3}{2}rac{N}{eta}+rac{N}{eta}-rac{NmgH}{\mathrm{e}^{eta mgH}-1}=U_0+NkT-rac{NmgH}{\mathrm{e}^{mgH/kT}-1}$$

热容

$$C_V = rac{\partial U}{\partial T} = C_V^0 + Nk - rac{N(mgH)^2 \mathrm{e}^{mgH/kT}}{(\mathrm{e}^{mgH/kT}-1)^2} rac{1}{kT^2}$$

7.18

解:

双原子分子中的相对振动可以看作线性谐振子,能级为

$$arepsilon_n = \left(n + rac{1}{2}
ight)\hbar\omega, \quad n = 0, 1, 2, \ldots$$

振动配分函数

$$Z_1^V = \sum_{n=0}^{+\infty} \mathrm{e}^{-eta\hbar\omega\left(n+rac{1}{2}
ight)} = rac{\mathrm{e}^{-rac{eta\hbar\omega}{2}}}{1-\mathrm{e}^{-eta\hbar\omega}}$$

故振动熵

$$egin{aligned} S^V &= Nk \left(\ln Z_1^V - eta rac{\partial}{\partial eta} \ln Z_1^V
ight) \ &= Nk \left[rac{eta \hbar \omega}{\mathrm{e}^{eta \hbar \omega} - 1} - \ln(1 - \mathrm{e}^{-eta \hbar \omega})
ight] \ &= Nk \left[rac{ heta_V/T}{\mathrm{e}^{ heta_V/T} - 1} - \ln(1 - \mathrm{e}^{- heta_V/T})
ight] \end{aligned}$$

其中 $heta_V=\hbar\omega/k$ 为振动特征温度。

7.19

解:

能级间距远小于 kT, 可以采用经典近似。转动配分函数

$$Z_1^r = \int \mathrm{e}^{-rac{eta}{2l}(p_ heta^2 + rac{1}{\sin^2 heta}p_arphi^2)} \, rac{\mathrm{d}p_ heta \mathrm{d}p_arphi \mathrm{d} heta \mathrm{d}arphi}{h^2} = rac{8\pi^2 I}{h^2eta}$$

故转动熵

$$egin{aligned} S^r &= Nk \left(\ln Z_1^r - eta rac{\partial}{\partial eta} \ln Z_1^r
ight) \ &= Nk \left(\ln rac{2I}{\hbar^2 eta} + 1
ight) \ &= Nk (\ln T/ heta_r + 1) \end{aligned}$$

其中 $\theta_r = \hbar^2/2Ik$ 为转动特征温度。

7.20

解:

爱因斯坦固体配分函数

$$Z_1 = \sum_{n=0}^{+\infty} \mathrm{e}^{-eta\hbar\omega\left(n+rac{1}{2}
ight)} = rac{\mathrm{e}^{-rac{eta\hbar\omega}{2}}}{1-\mathrm{e}^{-eta\hbar\omega}}$$

熵

$$egin{aligned} S &= 3Nk \left(\ln Z_1 - eta rac{\partial}{\partial eta} \ln Z_1
ight) \ &= 3Nk \left[rac{eta \hbar \omega}{\mathrm{e}^{eta \hbar \omega} - 1} - \ln(1 - \mathrm{e}^{-eta \hbar \omega})
ight] \ &= 3Nk \left[rac{ heta_E/T}{\mathrm{e}^{ heta_E/T} - 1} - \ln(1 - \mathrm{e}^{- heta_E/T})
ight] \end{aligned}$$

其中 $heta_E=\hbar\omega/k$ 为爱因斯坦特征温度。

解:

配分函数

$$Z_1 = \mathrm{e}^{-eta arepsilon_0} + \mathrm{e}^{-eta arepsilon_1} = \mathrm{e}^{-eta arepsilon_0} [1 + \mathrm{e}^{-eta (arepsilon_1 - arepsilon_0)}]$$

故内能

$$U=-Nrac{\partial}{\partialeta}\ln Z_1=Narepsilon_0+rac{N(arepsilon_1-arepsilon_0)}{1+\mathrm{e}^{eta(arepsilon_1-arepsilon_0)}}$$

熵

$$S = Nk \left(\ln Z_1 - eta rac{\partial}{\partial eta} \ln Z_1
ight) \ = Nk \left\{ \ln [1 + \mathrm{e}^{-eta(arepsilon_1 - arepsilon_0)}] + rac{eta(arepsilon_1 - arepsilon_0)}{1 + \mathrm{e}^{eta(arepsilon_1 - arepsilon_0)}}
ight\}$$

高温极限下

$$U=Nrac{arepsilon_1+arepsilon_0}{2},\quad S=Nk\ln 2$$

低温极限下

$$U=Narepsilon_0,\quad S=0$$

7.22

解:

原子磁矩在外磁场中的势能可能为 $0,\pm \mu B$ 。故配分函数

$$Z_1 = 1 + e^{\beta \mu B} + e^{-\beta \mu B} = 1 + 2 \cosh(\beta \mu B)$$

磁化强度

$$\mathscr{M} = rac{n}{eta} rac{\partial}{\partial B} \ln Z_1 = n \mu rac{2 \sinh eta \mu B}{1 + 2 \cosh eta \mu B}$$

弱场高温极限下 $\beta \mu B \ll 1$,

$$\mathscr{M} = rac{2}{3} rac{n\mu^2}{kT} B$$

强场低温极限下 $\beta \mu B \gg 1$,

$$\mathcal{M} = n\mu$$

7.23

证明:

根据公式

$$arepsilon^r = rac{1}{2I} \left(p_ heta^2 + rac{1}{\sin^2 heta} p_arphi^2
ight) - d_0 E \cos heta$$

经典转动配分函数

$$egin{aligned} Z_1^r &= \int \mathrm{e}^{-rac{eta}{2l}(p_ heta^2 + rac{1}{\sin^2 heta}p_arphi^2)} \mathrm{e}^{eta d_0 E\cos heta} \, rac{\mathrm{d}p_ heta \mathrm{d}p_arphi \mathrm{d} heta \mathrm{d}arphi}{h^2} \ &= rac{4\pi^2 I}{h^2eta} \int_0^\pi \mathrm{e}^{eta d_0 E\cos heta} \sin heta \, \mathrm{d} heta \ &= rac{I}{eta \hbar^2} rac{\mathrm{e}^{eta d_0 E} - \mathrm{e}^{-eta d_0 E}}{eta d_0 E} \end{aligned}$$

7.24

证明:

在高温极限下 $eta d_0 E \ll 1$,电极化强度

$$P=rac{n}{eta}rac{\partial}{\partial E}\ln Z_1=nd_0\left[rac{\mathrm{e}^{eta d_0E}+\mathrm{e}^{-eta d_0E}}{\mathrm{e}^{eta d_0E}-\mathrm{e}^{-eta d_0E}}-rac{1}{eta d_0E}
ight]pproxrac{nd_0^2}{3kT}E$$

6.12

8.1, 8.2, 8.3

证明:

对于理想波色系统,

$$\Omega = \prod_l rac{(\omega_l + a_l - 1)!}{a_l!(\omega_l - 1)!}
onumber \ \ln \Omega = \sum_l [(\omega_l + a_l - 1)\ln(\omega_l + a_l - 1) - a_l\ln a_l - (\omega_l - 1)\ln(\omega_l - 1)]$$

巨配分函数

$$\ln\Xi = -\sum_l \omega_l \ln(1-\mathrm{e}^{-lpha-etaarepsilon_l})$$

故熵

$$S = k \left(\ln \Xi - lpha rac{\partial}{\partial lpha} \ln \Xi - eta rac{\partial}{\partial eta} \ln \Xi
ight) \ = -k \sum_{l} \left[(\omega_{l} - 1) \ln rac{\omega_{l} - 1}{\omega_{l} - a_{l} - 1} + a_{l} \ln rac{\omega_{l} - a_{l} - 1}{a_{l}}
ight] \ = k \sum_{l} \left[(\omega_{l} + a_{l} - 1) \ln(\omega_{l} + a_{l} - 1) - a_{l} \ln a_{l} - (\omega_{l} - 1) \ln(\omega_{l} - 1)
ight] \ = k \ln \Omega$$

对于理想费米系统,

$$\Omega = \prod_l rac{\omega_l!}{a_l!(\omega_l - a_l)!} \ \ln \Omega = \sum_l [\omega_l \ln \omega_l - a_l \ln a_l - (\omega_l - a_l) \ln (\omega_l - a_l)]$$

巨配分函数

$$\ln\Xi = \sum_l \omega_l \ln(1+\mathrm{e}^{-lpha-etaarepsilon_l}) = \sum_l \omega_l \lnrac{\omega_l}{\omega_l-a_l}$$

故熵

$$S = k \left(\ln \Xi - lpha rac{\partial}{\partial lpha} \ln \Xi - eta rac{\partial}{\partial eta} \ln \Xi
ight) \ = k \sum_{l} \left(\omega_{l} \ln rac{\omega_{l}}{\omega_{l} - a_{l}} + a_{l} \ln rac{\omega_{l} - a_{l}}{a_{l}}
ight) \ = k \sum_{l} \left[\omega_{l} \ln \omega_{l} - a_{l} \ln a_{l} - (\omega_{l} - a_{l}) \ln (\omega_{l} - a_{l})
ight] = k \ln \Omega$$

证明:

对于理想费米系统,

$$egin{aligned} S_{ ext{F.D.}} &= k \sum_{l} [\omega_l \ln \omega_l - a_l \ln a_l - (\omega_l - a_l) \ln (\omega_l - a_l)] \ &= -k \sum_{l} \omega_l \left[\left(1 - rac{a_l}{\omega_l}
ight) \ln \left(1 - rac{a_l}{\omega_l}
ight) + rac{a_l}{\omega_l} \ln rac{a_l}{\omega_l}
ight] \ &= -k \sum_{l} [f_s \ln f_s + (1 - f_s) \ln (1 - f_s)] \end{aligned}$$

对于理想波色系统,

$$egin{aligned} S_{ ext{B.E.}} &= k \sum_{l} [(\omega_l + a_l - 1) \ln(\omega_l + a_l - 1) - a_l \ln a_l - (\omega_l - 1) \ln(\omega_l - 1)] \ &= -k \sum_{l} (\omega_l - 1) \left[\left(1 + rac{a_l}{\omega_l - 1}
ight) \ln \left(1 + rac{a_l}{\omega_l - 1}
ight) - rac{a_l}{\omega_l - 1} \ln rac{a_l}{\omega_l - 1}
ight] \ &= -k \sum_{l} [f_s \ln f_s - (1 + f_s) \ln(1 + f_s)] \end{aligned}$$

当 $f_s \ll 1$ 时,

\$\$

(1 - f_s) \ln (1 - f_s) \approx - f_s,;

• (1 + f_s) \ln (1 + f_s) \approx - f_s

故有

 $S_{\text{B.E.}} \sim S_{\text{B.E.}} \sim S_{\text{B.E.}} = - k \sim (f_s \in f_s)$

解:

弱简并费米 (波色) 气体的内能

$$U=rac{3}{2}NkT\left[1\pmrac{1}{4\sqrt{2}}rac{1}{g}rac{N}{V}\left(rac{h^2}{2\pi mkT}
ight)^{rac{3}{2}}
ight]$$

其中上面表示费米,下面表示波色。压强

$$p=rac{2}{3}rac{U}{V}=nkT\left[1\pmrac{1}{4\sqrt{2}}rac{1}{g}rac{N}{V}\left(rac{h^2}{2\pi mkT}
ight)^{rac{3}{2}}
ight]$$

定容热容

$$C_V = \left(rac{\partial U}{\partial T}
ight)_V = rac{3}{2}Nk\left[1\mprac{1}{8\sqrt{2}}rac{1}{g}rac{N}{V}\left(rac{h^2}{2\pi mkT}
ight)^rac{3}{2}
ight]$$

熵

$$egin{align} S &= \int rac{C_V}{T} \, \mathrm{d}T + S_0(V) \ &= rac{3}{2} N k \ln T \pm N k rac{1}{8\sqrt{2}} rac{1}{g} rac{N}{V} \left(rac{h^2}{2\pi m k T}
ight)^rac{3}{2} + S_0(V) \end{aligned}$$

根据理想极限, $N/V(h^2/2\pi mkT)^{3/2}\ll 1$,有

$$S=Nk\left[\ln ng\left(rac{2\pi mkT}{h^2}
ight)^{rac{3}{2}}+rac{5}{2}\pmrac{1}{8\sqrt{2}}rac{1}{g}rac{N}{V}\left(rac{h^2}{2\pi mkT}
ight)^{rac{3}{2}}
ight]$$

6.14

8.4, 8.5, 8.6, 8.8, 8.10, 8.11

证明:

二维自由粒子

$$\mathrm{d}n = D(\varepsilon)\mathrm{d}\varepsilon = rac{2\pi L^2}{h^2}m\mathrm{d}\varepsilon$$

假设临界温度 T_C 应满足

$$\int_0^{+\infty} \frac{D(\varepsilon) \, \mathrm{d}\varepsilon}{\mathrm{e}^{\varepsilon/kT_C} - 1} = n$$

$$rac{2\pi L^2}{h^2}mkT_C\int_0^{+\infty}rac{\mathrm{d}x}{\mathrm{e}^x-1}=n$$

但是上式中积分发散,故不存在这样的 T_C ,即二维理想波色气体不会发生波色-爱因斯坦凝聚。

8.5

证明:

三维谐振势场下原子能级

$$arepsilon(n_x,n_y,n_z)=\hbar\omega_x\left(n_x+rac{1}{2}
ight)+\hbar\omega_y\left(n_y+rac{1}{2}
ight)+\hbar\omega_z\left(n_z+rac{1}{2}
ight)$$

即 $arepsilon_0 = rac{1}{2}\hbar(\omega_x + \omega_y + \omega_z)$ 。当温度降到临界温度时,有

$$\sum_{n_x,n_y,n_z}rac{1}{\mathrm{e}^{rac{\hbar}{kT_C}(n_x\omega_x+n_y\omega_y+n_z\omega_z)}-1}=N$$

记 $\tilde{n}_x=\hbar\omega_x n_x/kT_C, \tilde{n}_y=\hbar\omega_y n_y/kT_C, \tilde{n}_z=\hbar\omega_z n_z/kT_C,$ 在 $N\to\infty,\bar{\omega}\to0$ 的情况下,变求和为积分,即

$$\left(rac{kT_C}{\hbarar{\omega}}
ight)^3\iiint rac{\mathrm{d}ar{n}_x\mathrm{d}ar{n}_y\mathrm{d}ar{n}_z}{\mathrm{e}^{ar{n}_x+ar{n}_y+ar{n}_z}-1}=N$$

上式中积分式的结果为 1.202。故

$$N=1.202\left(rac{kT_C}{\hbarar{\omega}}
ight)^3$$

当温度 $T < T_C$ 时,基态原子数

$$N-N_0=1.202\left(rac{kT_C}{\hbarar{\omega}}
ight)^3$$

即

$$rac{N_0}{N} = 1 - \left(rac{T}{T_C}
ight)^3$$

8.6

证明:

同上题,z方向上原子冻结在基态。故上题中三维改为二维情况。

$$\iint rac{\mathrm{d}ar{n}_x \mathrm{d}ar{n}_y}{\mathrm{e}^{ar{n}_x + ar{n}_y} - 1} = 1.645$$

故

$$N=1.645\left(rac{kT_C}{\hbarar{\omega}}
ight)^2$$

当温度 $T < T_C$ 时,基态原子数

$$N-N_0=1.645\left(rac{kT_C}{\hbarar{\omega}}
ight)^2$$

即

$$rac{N_0}{N} = 1 - \left(rac{T}{T_C}
ight)^2$$

证明:

辐射内能密度

$$u(\omega,T)\mathrm{d}\omega=rac{1}{\pi^2c^3}rac{\hbar\omega^3}{\mathrm{e}^{rac{\hbar\omega}{kT}}-1}\mathrm{d}\omega$$

根据 $\omega = 2\pi c/\lambda$,有

$$u_{\lambda}\mathrm{d}\lambda=rac{8\pi hc}{\lambda^{5}}rac{\mathrm{d}\lambda}{\mathrm{e}^{rac{hc}{\lambda kT}}-1}$$

令 $x = hc/\lambda kT$, 则极大值应该有

$$\frac{\mathrm{d}}{\mathrm{d}x} \left(\frac{x^5}{\mathrm{e}^x - 1} \right) = 0$$

即 λ_m 满足 $x_m = hc/\lambda_m kT$ 是

$$5\mathrm{e}^{-x} + x = 5$$

的根。这个根为 x = 4.9651。故

$$\lambda_m T = rac{hc}{4.9651k}$$

8.10

解:

根据光子气体内能,得到热容

$$C_V = \left(rac{\partial U}{\partial T}
ight)_V = rac{4\pi^2 k^4}{15c^3\hbar^3} V T^3$$

光子气体的熵

$$S = \int_0^T rac{C_V}{T} \, \mathrm{d}T = rac{4\pi^2 k^4}{15c^3\hbar^3} V \int_0^T T^2 \, \mathrm{d}T = rac{4\pi^2 k^4}{45c^3\hbar^3} V T^3$$

解:

根据辐射通量密度公式

$$J_u=rac{\pi^2k^4}{60c^2\hbar^3}T^4$$

当
$$T = 6000 \,\mathrm{K}$$
 时, $J_u = 7.14 \times 10^7 \,\mathrm{J} \cdot \mathrm{m}^{-2}$ 。
当 $T = 1000 \,\mathrm{K}$ 时, $J_u = 5.51 \times 10^4 \,\mathrm{J} \cdot \mathrm{m}^{-2}$ 。

6.19

8.17, 8.20, 8.22, 8.23, 8.24, 8.25

8.17

证明:

0 K 的费米气体压强

$$p=rac{2}{5}n\mu(0)=rac{2}{5}rac{\hbar^2}{2m}(3\pi^2N)^{rac{2}{3}}Nrac{1}{V}^{rac{5}{3}}$$

故

$$\left(rac{\partial p}{\partial V}
ight)_T = -rac{2}{3}rac{\hbar^2}{2m}(3\pi^2N)^{rac{2}{3}}Nrac{1}{V}^{rac{7}{3}} = -rac{2}{3}n\mu(0)rac{1}{V}$$

故等温压缩系数

$$\kappa_T = -rac{1}{V} \left(rac{\partial V}{\partial p}
ight)_T = rac{3}{2} rac{1}{n\mu(0)}$$

在T=0下,绝热压缩系数

$$\kappa_S = -rac{1}{V} \left(rac{\partial V}{\partial p}
ight)_S = -rac{1}{V} \left(rac{\partial V}{\partial p}
ight)_T = rac{3}{2} rac{1}{n\mu(0)}$$

解:

一级修正值

$$\mu(T) - \mu(0) = -\mu(0) \frac{\pi^2}{12} \left[\frac{kT}{\mu(0)} \right]^2 = -7.04 \times \frac{\pi^2}{12} \left[\frac{kT}{\mu(0)} \right]^2 = -7.88 \times 10^{-5} \, \mathrm{eV}$$

8.22

解:

粒子能级

$$arepsilon(n_x,n_y,n_z)=\hbar\omega_r(n_x+n_y+\lambda n_z)+rac{1}{2}\hbar\omega_r(2+\lambda)$$

取常数项为势能零点。由 $kT\gg\hbar\omega_r$,化学势有

$$N = \sum_{n_x,n_y,n_z} rac{1}{\mathrm{e}^{eta[\hbar\omega_r(n_x+n_y+\lambda n_z)-\mu]}+1} \ = \iiint rac{\mathrm{d}n_x \mathrm{d}n_y \mathrm{d}n_z}{\mathrm{e}^{eta[\hbar\omega_r(n_x+n_y+\lambda n_z)-\mu]}+1} \ = rac{1}{\lambda(\hbar\omega_r)^3} \int rac{arepsilon^2}{2} rac{\mathrm{d}arepsilon}{\mathrm{e}^{eta(arepsilon-\mu)}+1}$$

在绝对零度,有

$$N = \frac{1}{\lambda(\hbar\omega_r)^3} \int_0^{\mu(0)} \frac{\varepsilon^2}{2} d\varepsilon = \frac{1}{\lambda(\hbar\omega_r)^3} \frac{\mu^3(0)}{6}$$

故化学势

$$\mu(0)=\hbar\omega_r(6\lambda N)^{rac{1}{3}}$$

平均能量

$$ar{arepsilon} = rac{1}{N} rac{1}{\lambda (\hbar \omega_r)^3} \int_0^{\mu(0)} rac{arepsilon^2}{2} arepsilon \, \mathrm{d}arepsilon = rac{3}{4} \mu(0)$$

代入数值得

$$\mu(0) = 2.98 \times 10^{-10} \,\mathrm{eV}$$

 $\bar{\varepsilon} = 2.24 \times 10^{-10} \,\mathrm{eV}$

8.23

解:

低温极限下,

$$N = rac{1}{\lambda(\hbar\omega_r)^3} \int_0^{+\infty} rac{arepsilon^2}{2} rac{\mathrm{d}arepsilon}{\mathrm{e}^{rac{arepsilon-\mu}{kT}} + 1} \ pprox rac{1}{\lambda(\hbar\omega_r)^3} rac{\mu^3}{6} \left[1 + \pi^2 \left(rac{kT}{\mu}
ight)^2
ight]$$

故有化学势

$$\mupprox\mu(0)\left\{1-rac{\pi^2}{3}\left[rac{kT}{\mu(0)}
ight]^2
ight\}$$

内能

$$U = rac{1}{\lambda(\hbar\omega_r)^3} \int_0^{+\infty} rac{arepsilon^2}{2} rac{arepsilon \mathrm{d}arepsilon}{\mathrm{e}^{rac{arepsilon-\mu}{kT}} + 1} \ pprox rac{3}{4} N \mu(0) \left\{ 1 + rac{2\pi^2}{3} \left[rac{kT}{\mu(0)}
ight]^2
ight\}$$

热容

$$C = \frac{\mathrm{d}U}{\mathrm{d}T} = Nk\pi^2 \frac{kT}{\mu(0)}$$

在高温极限下,费米气体近似非简并,故采用玻尔兹曼统计。配分函数

$$Z_1 = rac{1}{\lambda(\hbar\omega_r)^3} \int_0^{+\infty} rac{arepsilon^2}{2} \mathrm{e}^{-etaarepsilon} \, \mathrm{d}arepsilon = rac{1}{\lambda(\hbar\omega_r)^3} rac{1}{eta^3}$$

化学势

$$\mu = -kT \ln rac{Z_1}{N} = -kT \ln 6 \left[rac{kT}{\mu(0)}
ight]^3$$

内能

$$U = -N rac{\partial}{\partial eta} \ln Z_1 = 3NkT$$

8.24

解:

简并费米气体密度

$$n = rac{A/2}{rac{4}{3}\pi(1.3 imes10^{-15})^3A} = rac{3}{8}\pirac{1}{(1.3 imes10^{-15})^3}\,\mathrm{m}^{-3}$$

$$\mu(0) = rac{\hbar^2}{2m} (3\pi^2 n)^{rac{2}{3}} = 0.43 imes 10^{-11} \, \mathrm{J}$$

平均动能

$$ar{arepsilon} = rac{3}{5} \mu(0) = 0.26 imes 10^{-11} \, \mathrm{J}$$

8.25

解:

$$\mu(0)=rac{\hbar^2}{2m}(3\pi^2n)^{rac{2}{3}}$$

热容

$$C_V = Nkrac{\pi^2}{2}rac{kT}{\mu(0)} = rac{\pi^2}{\hbar^2}rac{m^*kT}{(3\pi^2n)^{rac{2}{3}}} = 2.89NkT$$

故有有效质量

$$m^*pprox 3m$$

6.21

9.1, 9.3, 9.4, 9.5, 9.6, 9.15, 9.16, 9.19, 9.21, 9.22

9.1

证明:

根据 $\rho_s = 1/\Omega$,有熵

$$S=k\ln\Omega=k\sum_{s}
ho_{s}\ln\Omega=-k\sum_{s}
ho_{s}\ln
ho_{s}$$

9.3

解:

N个单原子分子气体

$$E=\sum_{i=1}^{3N}rac{p_i^2}{2m}$$

配分函数

$$egin{aligned} Z &= rac{1}{N!h^{3N}} \int \mathrm{e}^{-eta E} \, \mathrm{d}\Omega \ &= rac{V^N}{N!h^{3N}} \prod_{i=1}^{3N} \int \mathrm{e}^{-eta rac{p_i^2}{2m}} \, \mathrm{d}p_i \ &= rac{V^N}{N!h^{3N}} \left(rac{2\pi m}{eta}
ight)^{rac{3N}{2}} \end{aligned}$$

压强

$$p = rac{1}{eta} rac{\partial}{\partial V} \ln Z = rac{N}{V eta} = rac{NkT}{V}$$

$$pV = NkT$$

内能

$$U = -\frac{\partial}{\partial \beta} \ln Z = \frac{3N}{2} kT$$

熵

$$S = k \left(\ln Z - eta rac{\partial}{\partial eta} \ln Z
ight) \ = N k \left[rac{3}{2} \ln rac{2\pi m k T}{h^2} + \ln rac{V}{N} + rac{5}{2}
ight]$$

化学势

$$\mu = -kT \ln Z = -kT \left[rac{3}{2} \ln rac{2\pi m kT}{h^2} + \ln rac{V}{N}
ight]$$

9.4

解:

对于单原子分子,有

$$C_V = rac{3}{2}Nk$$

故能量相对涨落

$$rac{(E - ar{E})^2}{ar{E}^2} = rac{kT^2C_V}{ar{E}^2} = rac{2}{3N}$$

对于双原子分子,有

$$C_V=rac{5}{2}Nk$$

故能量相对涨落

$$rac{(E - ar{E})^2}{ar{E}^2} = rac{kT^2C_V}{ar{E}^2} = rac{2}{5N}$$

解:

混合气体能量

$$E = \sum_{i=1}^{3N_A} rac{p_{Ai}^2}{2m_A} + \sum_{i=1}^{3N_B} rac{p_{Bi}^2}{2m_B}$$

配分函数

$$Z = rac{1}{N_A!N_B!h^{3N_A}h^{3N_B}}\int \mathrm{e}^{-eta E}\,\mathrm{d}\Omega \ = rac{1}{N_A!h^{3N_A}}\int \mathrm{e}^{-eta E}\,\mathrm{d}\Omega + rac{1}{N_B!h^{3N_A}}\int \mathrm{e}^{-eta E}\,\mathrm{d}\Omega_B \ = Z_AZ_B$$

故物态方程

$$pV = (N_A + N_B)kT$$

内能

$$U=-rac{\partial}{\partialeta}\ln Z=rac{3}{2}(N_A+N_B)kT$$

熵

$$S = k \left(\ln Z - eta rac{\partial}{\partial eta} \ln Z
ight) \ = N_A k \left[rac{3}{2} \ln rac{2\pi m_A k T}{h^2} + \ln rac{V}{N_A} + rac{5}{2}
ight] + N_B k \left[rac{3}{2} \ln rac{2\pi m_B k T}{h^2} + \ln rac{V}{N_B} + rac{5}{2}
ight]$$

9.6

解:

极端相对论气体能量

$$E = \sum_{i=1}^{3N} c p_i$$

配分函数

$$Z = rac{1}{N!h^{3N}} \int \mathrm{e}^{-eta E} \, \mathrm{d}\Omega$$
 $= rac{V^N}{N!} \prod_{i=1}^N rac{1}{h^3} \int \mathrm{e}^{-eta c p_i} \, \mathrm{d}ec{p}_i$
 $= rac{V^N}{N!} \left[8\pi \left(rac{kT}{hc}
ight)^3
ight]^N$

压强

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z = \frac{N}{V\beta} = \frac{NkT}{V}$$

即物态方程

$$pV = NkT$$

内能

$$U = -rac{\partial}{\partialeta}\ln Z = 3NkT$$

熵

$$S = k \left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \right)$$

$$= Nk \left[3 \ln \frac{kT}{hc} + \ln \frac{8\pi V}{N} + 4 \right]$$

化学势

$$\mu = -kT \ln Z = -kT \left[3 \ln rac{kT}{hc} + \ln rac{8\pi V}{N}
ight]$$

解:

巨配分函数

$$egin{aligned} \Xi &= \sum_{N=0}^{+\infty} \sum_{s} \mathrm{e}^{-lpha N - eta E_{s}} = \sum_{N=0}^{+\infty} \mathrm{e}^{-lpha N} Z_{N} \ &= \sum_{N=0}^{+\infty} rac{1}{N!} \left[\mathrm{e}^{-lpha} V \left(rac{2\pi m}{eta h^{2}}
ight)^{rac{3}{2}}
ight]^{N} \ &= \exp \left[\mathrm{e}^{-lpha} V \left(rac{2\pi m}{eta h^{2}}
ight)^{rac{3}{2}}
ight] \end{aligned}$$

故气体的平均粒子数

$$ar{N} = -rac{\partial}{\partial lpha} \ln \Xi = \mathrm{e}^{-lpha} V \left(rac{2\pi m}{eta h^2}
ight)^{rac{3}{2}}$$

得

$$lpha = \ln \left[rac{V}{ar{N}} \left(rac{2\pi m}{eta h^2}
ight)^{rac{3}{2}}
ight]$$

压强

$$p=rac{1}{eta}rac{\partial}{\partial V}\ln\Xi=rac{kT}{V}ar{N}$$

即物态方程

$$pV=ar{N}kT$$

内能

$$U = -\frac{\partial}{\partial eta} \ln \Xi = \frac{3}{2} \bar{N} k T$$

熵

$$S = k \left(\ln \Xi - \alpha \frac{\partial}{\partial \alpha} \ln \Xi - \beta \frac{\partial}{\partial \beta} \ln \Xi \right)$$

= $\bar{N}k \left(\alpha + \frac{5}{2} \right)$

化学势

$$\mu = -kTlpha = -kT\ln\left[rac{V}{ar{N}}\left(rac{2\pi m}{eta h^2}
ight)^{rac{3}{2}}
ight]$$

9.16

解:

单原子和双原子理想气体物态方程均有 $pV=ar{N}kT$,故

$$\left(rac{\partial V}{\partial p}
ight)_{ar{N},T} = -rac{ar{N}kT}{p^2}$$

粒子数相对涨落

$$rac{(N-ar{N})^2}{ar{N}^2} = -rac{kT}{V^2} \left(rac{\partial V}{\partial p}
ight)_{ar{N},T} = rac{1}{ar{N}}$$

9.19

解:

巨配分函数

$$egin{aligned} \Xi &= \sum_{N=0}^{+\infty} \sum_{s} \mathrm{e}^{-lpha N - eta E_{s}} = \sum_{N=0}^{+\infty} \mathrm{e}^{-lpha N} Z_{N} \ &= \sum_{N=0}^{+\infty} rac{1}{N!} \left[\mathrm{e}^{-lpha} A \left(rac{2\pi m}{eta h^{2}}
ight) \mathrm{e}^{eta arepsilon_{0}}
ight]^{N} \ &= \exp \left[\mathrm{e}^{-lpha} A \left(rac{2\pi m}{eta h^{2}}
ight) \mathrm{e}^{eta arepsilon_{0}}
ight] \end{aligned}$$

$$ar{N} = -rac{\partial}{\partial lpha} \ln \Xi = \mathrm{e}^{-lpha} A \left(rac{2\pi m}{eta h^2}
ight) \mathrm{e}^{eta arepsilon_0} = A \left(rac{2\pi m k T}{h^2}
ight) \mathrm{e}^{rac{arepsilon_0 + \mu}{k T}}$$

单原子分子化学势

$$\mu = hT \ln \left[rac{p}{kT} \left(rac{h^2}{2\pi m kT}
ight)^rac{3}{2}
ight]$$

故吸附分子的面密度为

$$rac{ar{N}}{A} = rac{p}{kT} \left(rac{h^2}{2\pi m k T}
ight)^{rac{1}{2}} \mathrm{e}^{rac{arepsilon_0}{kT}}$$

9.21

证明:

玻尔兹曼分布

$$ar{a}_l = \omega_l \mathrm{e}^{-lpha - eta arepsilon_l}$$

粒子数涨落

$$(a_l - \bar{a}_l)^2 = -rac{\partial ar{a}_l}{\partial lpha} = ar{a}_l$$

9.22

证明:

光子气体有 $\alpha=0$,故巨配分函数

$$\Xi = \sum_{a_l} \mathrm{e}^{-eta arepsilon_l a_l}$$

平均粒子数

$$ar{a}_l = rac{\sum_{a_l} a_l \mathrm{e}^{-eta arepsilon_l a_l}}{\sum_{a_l} \mathrm{e}^{-eta arepsilon_l a_l}}$$

$$-rac{1}{eta}rac{\partialar{a}_l}{\partialarepsilon_l} = rac{\sum_{a_l}a_l^2\mathrm{e}^{-etaarepsilon_la_l}}{\sum_{a_l}\mathrm{e}^{-etaarepsilon_la_l}} - rac{(\sum_{a_l}a_l\mathrm{e}^{-etaarepsilon_la_l})^2}{(\sum_{a_l}\mathrm{e}^{-etaarepsilon_la_l})^2} = (a_l - ar{a}_l)^2$$

又光子气体有

$$ar{a}_l = rac{1}{\mathrm{e}^{etaarepsilon_l}-1}$$

故

$$(a_l$$
 $\stackrel{-}{-}$ $ar{a}_l)^2=ar{a}_l(1+ar{a}_l)$

6.23

9.7, 9.8, 9.13, 9.14

9.7

解:

实际气体能量

$$E = \sum_{i=1}^N rac{p_i^2}{2m} + \sum_{i < j} \phi(r_{ij})$$

动量分布概率

$$f(p_j)\,\mathrm{d} p_j = rac{\mathrm{e}^{-etarac{p_j^2}{2m}}\,\mathrm{d} p_j}{\int \mathrm{e}^{-etarac{p_j^2}{2m}}\,\mathrm{d} p_j} = \left(rac{1}{2\pi m k T}
ight)^{rac{3}{2}} \mathrm{e}^{-etarac{p_j^2}{2m}}\,\mathrm{d} p_j$$

故速度分布律

$$f(ec{v})\,\mathrm{d}ec{v} = \left(rac{m}{2\pi kT}
ight)^{rac{3}{2}}\mathrm{e}^{-rac{m}{2kT}ec{v}^2}\,\mathrm{d}ec{v}$$

9.8

证明:

二维气体能量

$$E = \sum_{i=1}^{2N} rac{p_i^2}{2m} + \sum_{i < j} \phi(r_{ij})$$

配分函数

$$Z=rac{1}{N!h^{2N}}\int \mathrm{e}^{-eta E}\,\mathrm{d}\Omega=rac{1}{N!}\left(rac{2\pi m}{eta h^2}
ight)^NQ^{-1}$$

定义函数

$$f_{ij}=\mathrm{e}^{-eta\phi(r_{ij})}-1$$

位形积分

$$egin{aligned} Q &= \int \mathrm{e}^{-eta \sum_{i < j} \phi(r_{ij})} \, \mathrm{d}^N ec{r} \ &pprox \int (1 + \sum_{i < j} f_{ij}) \, \mathrm{d}^N ec{r} \ &pprox A^N \left[1 + rac{N^2}{2A} \int_0^{+\infty} (\mathrm{e}^{-eta \phi(r)} - 1) 2\pi r \, \mathrm{d}r
ight] \ &= A^N \left(1 - rac{N^2}{N_A A} B
ight) \end{aligned}$$

其中

$$B = -rac{N_A}{2} \int_0^{+\infty} ({
m e}^{-eta\phi(r)} - 1) 2\pi r \, {
m d}r$$

代入配分函数,得

$$pA = Arac{1}{eta}rac{\partial}{\partial V}\ln Z = rac{NkT}{A}\left(1 + rac{N}{N_AA}B
ight)$$

9.13

解:

平均场近似下, 弱场高温下, 顺磁体磁化强度

$$egin{aligned} M &= n \mu anh rac{\mu ar{B}}{kT} pprox n \mu rac{\mu ar{B}}{kT} \ &= rac{n \mu^2}{kT} B + rac{n \mu ar{\sigma}}{kT} Z J \ &= rac{n \mu^2}{kT} B + rac{M}{kT} Z J \ &= rac{n \mu^2 \mu_0}{k(T - Z J/k)} H \ &= rac{C}{T - heta} H \end{aligned}$$

解:

用平均场表示其他分子对单个分子的作用,有

$$E = \sum_{i=1}^N \left[rac{p_i^2}{2m} + \phi(ec{r}_i)
ight]$$

记位形积分

$$Z_1 = \int \mathrm{e}^{-eta\phi(r)}\,\mathrm{d}ec{r}$$

除去钢球体积 $ilde{V}$,相互作用用平均 ϕ 表示。设

$$ilde{V}=rac{N}{N_A}b, \quad \phi=-rac{a}{N_A^2}rac{N}{V}$$

故

$$Z_1 = (V - ilde{V}) \mathrm{e}^{-eta \phi}$$

则气体压强

$$p = rac{1}{eta} rac{\partial}{\partial V} \ln Z = NkT rac{\partial}{\partial V} \ln Z_1 \ = rac{NkT}{V - rac{N}{N_A} b} - rac{N^2}{N_A^2} rac{a}{V^2}$$

即得范德瓦尔斯方程

$$\left(p+rac{n^2a}{V^2}
ight)(V-nb)=NkT$$