热力学与统计物理

Charles

2025 年 1 月 9 日

目录

1 热力学的基本规律

1.1 热力学第零定律

1. 平衡态：在没有外界影响的条件下，物体各部分的性质长时间内不发生任何变化的状态
2. 热力学第零定律：若两个热力学系统均与第三个系统处于热平衡状态，此两个系统也必处于热平衡

1.2 物态方程

1. 三个系数：

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad \beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V, \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{1.1}$$

关系：

$$\alpha = \kappa_T \beta p \tag{1.2}$$

$$\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p = -1 \tag{1.3}$$

2. 理想气体：

$$pV = nRT \tag{1.4}$$

3. Van der Waals 气体：

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{1.5}$$

4. Onnes 方程：

$$pV = nRT\left(1 + A_2 p + A_3 p^2 + \cdots\right) \tag{1.6}$$

$$pV = nRT\left(1 + B_2 V^{-1} + B_3 V^{-2} + \cdots\right) \tag{1.7}$$

5. 流体与各向同性固体：

$$V = V_0\left(1 + \alpha(T - T_0) - \kappa_T(p - p_0)\right) \tag{1.8}$$

6. 顺磁固体：

$$\mathscr{M} = \frac{C}{T}\mathscr{H} \tag{1.9}$$

1.3 热力学第一定律

1. 热力学第一定律：

$$\mathrm{d}U = \text{đ}Q + \text{đ}W \tag{1.10}$$

2. 功：

$$\text{đ}W = \sum_i Y_i \mathrm{d}y_i \tag{1.11}$$

(1) 流体体积变化：

$$\text{đ}W = -p\mathrm{d}V \tag{1.12}$$

(2) 二维表面面积变化：

$$\text{đ}W = \sigma \mathrm{d}S \tag{1.13}$$

(3) 电介质极化：

$$\text{đ}W = V\mathscr{E}\cdot\mathrm{d}\mathscr{D} = V\mathrm{d}\left(\frac{1}{2}\varepsilon_0\mathscr{E}^2\right) + V\mathscr{E}\cdot\mathrm{d}\mathscr{P} \tag{1.14}$$

(4) 磁介质磁化：

$$\text{đ}W = V\mathscr{H}\cdot\mathrm{d}\mathscr{B} = V\mathrm{d}\left(\frac{1}{2}\mu_0\mathscr{H}^2\right) + \mu_0 V\mathscr{H}\cdot\mathrm{d}\mathscr{M} \tag{1.15}$$

3. 焓:

$$H = U + pV \tag{1.16}$$

4. 热容:

$$C = \frac{đQ}{\mathrm{d}T} \tag{1.17}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \quad C_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{1.18}$$

1.4 理想气体过程

1. 等容过程:

$$Q = \Delta U = \int_{T_1}^{T_2} C_V \mathrm{d}T \tag{1.19}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{i}{2}nR \tag{1.20}$$

$$\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{p}\frac{nR}{V} = \frac{1}{T} \tag{1.21}$$

2. 准静态的等压过程:

$$Q = \Delta H = \int_{T_1}^{T_2} C_p \mathrm{d}T \tag{1.22}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \frac{i+2}{2}nR \tag{1.23}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\frac{nR}{T} = \frac{1}{T} \tag{1.24}$$

3. 准静态的等温过程:

$$Q = -W = \int_{V_1}^{V_2} p \mathrm{d}V = nRT\ln\frac{V_1}{V_2} \tag{1.25}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{p} \tag{1.26}$$

4. 准静态的绝热过程:

$$\gamma = \frac{C_p}{C_V} = 1 + \frac{nR}{C_V} = \frac{i+2}{i}, \quad C_V = \frac{1}{\gamma-1}nR, \quad C_p = \frac{\gamma}{\gamma-1}nR \tag{1.27}$$

$$pV^\gamma = C, \quad TV^{\gamma-1} = C', \quad p^{\gamma-1}T^{-\gamma} = C'' \tag{1.28}$$

$$W = \int_{V_1}^{V_2} p\mathrm{d}V = \frac{1}{\gamma-1}(p_2V_2 - p_1V_1) \tag{1.29}$$

$$\alpha_s = -\frac{1}{\gamma-1}\frac{1}{T}, \quad \beta_s = \frac{\gamma}{\gamma-1}\frac{1}{T}, \quad \kappa_s = \frac{1}{\gamma}\frac{1}{p} \tag{1.30}$$

5. 准静态的多方过程:

$$pV^n = C, \quad TV^{n-1} = C', \quad p^{n-1}T^{-n} = C'' \tag{1.31}$$

$$C_n = \left(\frac{1}{\gamma-1} - \frac{1}{n-1}\right)nR \tag{1.32}$$

6. 热机效率:

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \leqslant 1 - \frac{T_L}{T_H} \tag{1.33}$$

7. 制冷系数:

$$\eta_c = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \leqslant \frac{T_L}{T_H - T_L} \tag{1.34}$$

8. 制热系数:

$$\eta_h = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} \leqslant \frac{T_H}{T_H - T_L} \tag{1.35}$$

1.5 热力学第二定律

1. 热力学第二定律：
   (1) Kelvin 表述：不可能从单一热源吸热使之完全变为有用功而不产生其他影响
   (2) Clausius 表述：热量不可能自发地从低温物体传到高温物体而不产生其他影响
2. Carnot 定理：所有工作于两个一定温度之间的热机，可逆机的效率最大
3. Carnot 定理推论：所有工作于两个一定温度之间的可逆机效率相等
4. 熵：
$$\mathrm{d}S = \frac{\text{đ}Q}{T} \tag{1.36}$$
5. Clausius 不等式：
$$\oint \frac{\text{đ}Q}{T} \leqslant 0 \tag{1.37}$$
6. 热力学第二定律的数学表述：
$$\Delta S \geqslant \int_i^f \frac{\text{đ}Q}{T} \tag{1.38}$$
7. 熵增原理：系统的熵在绝热过程中永不减少
8. 最大功定理：可逆过程输出的功最大

1.6 热力学基本方程

1. 热力学基本方程：
$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \tag{1.39}$$
2. Helmholtz 自由能：
$$F \equiv U - TS \tag{1.40}$$
3. 等温过程 Helmholtz 自由能的性质：
$$\Delta F \leqslant W, \quad W' \leqslant -\Delta F \tag{1.41}$$
4. Gibbs 函数：
$$G \equiv F + pV = H - TS = U - TS + pV \tag{1.42}$$
5. 等温等压过程 Gibbs 自由能的性质：
$$\Delta G \leqslant W_1, \quad W_1' \leqslant -\Delta G \tag{1.43}$$

2 均匀系的平衡性质

2.1 Maxwell 关系

1. 特性函数：

$$\mathrm{d}U(S,V)=T\mathrm{d}S-p\mathrm{d}V \tag{2.1}$$

$$\mathrm{d}H(S,p)=T\mathrm{d}S+V\mathrm{d}p \tag{2.2}$$

$$\mathrm{d}F(T,V)=-S\mathrm{d}T-p\mathrm{d}V \tag{2.3}$$

$$\mathrm{d}G(T,p)=-S\mathrm{d}T+V\mathrm{d}p \tag{2.4}$$

2. Maxwell 关系：

$$\left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial p}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial p}\right)_S=\left(\frac{\partial V}{\partial S}\right)_p \tag{2.5}$$

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial p}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_p \tag{2.6}$$

3. 热容关系：

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=T\left(\frac{\partial S}{\partial T}\right)_V, \quad C_p=\left(\frac{\partial H}{\partial T}\right)_p=T\left(\frac{\partial S}{\partial T}\right)_p \tag{2.7}$$

$$C_p-C_V=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p=VT\frac{\alpha^2}{\kappa_T} \tag{2.8}$$

理想气体：

$$C_p-C_V=nR \tag{2.9}$$

4. 变化率关系：

$$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V-p \tag{2.10}$$

$$\left(\frac{\partial H}{\partial p}\right)_T=V-T\left(\frac{\partial V}{\partial T}\right)_p \tag{2.11}$$

2.2 热力学函数

1. 基本热力学函数：

(1) (T,V) 为独立变量：

$$p=p(T,V) \tag{2.12}$$

$$U(T,V)=\int_{T_0}^{T}C_V\mathrm{d}T+\int_{V_0}^{V}\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]\mathrm{d}V+U_0 \tag{2.13}$$

$$S(T,V)=\int_{T_0}^{T}\frac{C_V}{T}\mathrm{d}T+\int_{V_0}^{V}\left(\frac{\partial p}{\partial T}\right)_V\mathrm{d}V+S_0 \tag{2.14}$$

(2) (T,p) 为独立变量：

$$V=V(T,p) \tag{2.15}$$

$$H(T,p)=\int_{T_0}^{T}C_p\mathrm{d}T+\int_{p_0}^{p}\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p+H_0 \tag{2.16}$$

$$S(T,p)=\int_{T_0}^{T}\frac{C_p}{T}\mathrm{d}T-\int_{p_0}^{p}\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}p+S_0 \tag{2.17}$$

2. 理想气体的热力学函数:

$$pv = RT \tag{2.18}$$

$$u = \int c_v \mathrm{d}T + u_0 \tag{2.19}$$

$$h = \int c_p \mathrm{d}T + h_0 \tag{2.20}$$

$$s = \int \frac{c_v}{T}\mathrm{d}T + R\ln v + s_0 = \int \frac{c_p}{T}\mathrm{d}T - R\ln p + s_0' \tag{2.21}$$

$$\mu = RT\left(\varphi(T) + \ln p\right), \quad \varphi(T) = \frac{h_0}{RT} - \int \frac{\mathrm{d}T}{RT^2}\int c_p \mathrm{d}T - \frac{s_0'}{R} \tag{2.22}$$

热容看作常数:

$$u = c_v T + u_0 \tag{2.23}$$

$$h = c_p T + h_0 \tag{2.24}$$

$$s = c_v \ln T + R\ln v + s_0 = c_p \ln T - R\ln p + s_0' \tag{2.25}$$

$$\mu = RT\left(\varphi(T) + \ln p\right), \quad \varphi(T) = \frac{h_0}{RT} - \frac{c_p}{R}\ln T + \frac{c_p - s_0'}{R} \tag{2.26}$$

3. Van der Waals 气体的热力学函数:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{2.27}$$

$$u = \int c_v \mathrm{d}T - \frac{a}{v} + u_0 \tag{2.28}$$

$$s = \int \frac{c_v}{T}\mathrm{d}T + R\ln v - b + s_0 \tag{2.29}$$

2.3 特性函数

1. 自由能是特性函数:

$$\mathrm{d}F(T,V) = -S\mathrm{d}T - p\mathrm{d}V \tag{2.30}$$

$$S(T,V) = -\left(\frac{\partial F}{\partial T}\right)_V \tag{2.31}$$

$$p(T,V) = -\left(\frac{\partial F}{\partial V}\right)_T \tag{2.32}$$

$$U(T,V) = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right) \tag{2.33}$$

2. Gibbs 函数是特性函数:

$$\mathrm{d}G(T,p) = -S\mathrm{d}T + V\mathrm{d}p \tag{2.34}$$

$$S(T,p) = -\left(\frac{\partial G}{\partial T}\right)_p \tag{2.35}$$

$$V(T,p) = \left(\frac{\partial G}{\partial p}\right)_T \tag{2.36}$$

$$U(T,p) = G - T\left(\frac{\partial G}{\partial T}\right)_p - p\left(\frac{\partial G}{\partial p}\right)_T \tag{2.37}$$

$$H(T,p) = G - T\left(\frac{\partial G}{\partial T}\right)_p = -T^2\frac{\partial}{\partial T}\left(\frac{G}{T}\right) \tag{2.38}$$

2.4 气体的节流过程

1. 节流过程：

$$H_1 = H_2 \tag{2.39}$$

2. Joule-Thomson 系数：

$$\mu \equiv \left(\frac{\partial T}{\partial p}\right)_H \tag{2.40}$$

$$\mu = -\left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] = \frac{V}{C_p}(T\alpha - 1) \tag{2.41}$$

2.5 平衡热辐射场的热力学理论

1. 辐射压强与内能密度的关系：

$$p = \frac{1}{3}u \tag{2.42}$$

2. 热辐射的热力学函数：

$$u = T\frac{1}{3}\frac{\mathrm{d}u}{\mathrm{d}T} - \frac{u}{3} \Rightarrow u(T) = aT^4 \tag{2.43}$$

$$p(T) = \frac{1}{3}aT^4 \tag{2.44}$$

$$U(T,V) = aT^4V \tag{2.45}$$

$$S(T,V) = \frac{4}{3}aT^3V \tag{2.46}$$

$$G(T,V) = 0 \tag{2.47}$$

3. 热辐射的热容：

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = 4aT^3V = 3S \tag{2.48}$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \infty \tag{2.49}$$

4. 热辐射的可逆绝热过程方程：

$$VT^3 = C, \quad pV^{4/3} = C' \tag{2.50}$$

5. 热辐射的辐射通量密度：

$$J = \frac{1}{4}cu = \frac{1}{4}caT^4 = \sigma T^4 \tag{2.51}$$

2.6 磁介质的热力学理论

1. 磁介质体积不变的热力学基本方程：

$$\mathrm{d}G = -S\mathrm{d}T - \mu_0 m\mathrm{d}\mathscr{H} \tag{2.52}$$

$$\left(\frac{\partial S}{\partial \mathscr{H}}\right)_T = \mu_0\left(\frac{\partial m}{\partial T}\right)_{\mathscr{H}} \tag{2.53}$$

2. 磁介质的热容：

$$C_{\mathscr{H}} = T\left(\frac{\partial S}{\partial T}\right)_{\mathscr{H}} \tag{2.54}$$

3. 绝热去磁致冷：

$$\left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_{\mathscr{H}}\left(\frac{\partial S}{\partial \mathscr{H}}\right)_T = -\frac{\mu_0 T}{C_{\mathscr{H}}}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} = \frac{\mu_0 C}{TC_{\mathscr{H}}}\mathscr{H} > 0 \tag{2.55}$$

4. 磁介质体积改变的热力学基本方程：

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p - \mu_0 m\mathrm{d}\mathscr{H} \tag{2.56}$$

$$\left(\frac{\partial V}{\partial \mathscr{H}}\right)_{T,p} = -\mu_0\left(\frac{\partial m}{\partial p}\right)_{T,\mathscr{H}} \tag{2.57}$$

3 单元系的复相平衡

3.1 粒子数可变系统

1. 化学势：

$$\mu \equiv u - Ts + pv \tag{3.1}$$

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V} = \left(\frac{\partial H}{\partial n}\right)_{S,p} = \left(\frac{\partial F}{\partial n}\right)_{T,V} = \left(\frac{\partial G}{\partial n}\right)_{T,p} \tag{3.2}$$

2. 粒子数可变的热力学基本方程：

$$\mathrm{d}U(S,V,n) = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}n \tag{3.3}$$

$$\mathrm{d}H(S,p,n) = T\mathrm{d}S + V\mathrm{d}p + \mu\mathrm{d}n \tag{3.4}$$

$$\mathrm{d}F(T,V,n) = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}n \tag{3.5}$$

$$\mathrm{d}G(T,p,n) = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}n \tag{3.6}$$

3. Gibbs-Duhem 关系：

$$\mathrm{d}\mu = -s\mathrm{d}T + v\mathrm{d}p \tag{3.7}$$

4. 巨势：

$$J = F - \mu\nu = U - TS - \mu n \tag{3.8}$$

$$\mathrm{d}J = -S\mathrm{d}T - p\mathrm{d}V - n\mathrm{d}\mu \tag{3.9}$$

3.2 热动平衡条件

1. 热动平衡判据：

$$S = S_{\max} \Longleftrightarrow \delta S = 0,\ \delta^2 S < 0,\ \delta U = 0,\ \delta V = 0,\ \delta n = 0 \tag{3.10}$$

$$F = F_{\min} \Longleftrightarrow \delta F = 0,\ \delta^2 F > 0,\ \delta T = 0,\ \delta V = 0,\ \delta n = 0 \tag{3.11}$$

$$G = G_{\min} \Longleftrightarrow \delta G = 0,\ \delta^2 G > 0,\ \delta T = 0,\ \delta p = 0,\ \delta n = 0 \tag{3.12}$$

$$U = U_{\min} \Longleftrightarrow \delta U = 0,\ \delta^2 U > 0,\ \delta V = 0,\ \delta S = 0,\ \delta n = 0 \tag{3.13}$$

2. 热动平衡条件：

$$T_\alpha = T, \quad p_\alpha = p, \quad \mu_\alpha = \mu \tag{3.14}$$

3. 热动平衡稳定条件：

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V > 0, \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T > 0 \tag{3.15}$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p > 0, \quad \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S > 0 \tag{3.16}$$

3.3 单元系的复相平衡

1. 二相平衡曲线：

$$\mu^\alpha(T,p) = \mu^\beta(T,p) \tag{3.17}$$

2. 相变潜热：

$$L_{\beta\alpha} = T(s^\beta - s^\alpha) = h^\beta - h^\alpha \tag{3.18}$$

3. Clapeyron 方程：

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{s^\beta - s^\alpha}{v^\beta - v^\alpha} = \frac{L_{\beta\alpha}}{T(v^\beta - v^\alpha)} \tag{3.19}$$

4. Kirchhoff 蒸汽压方程:

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{L}{T(v-v')}\approx\frac{L}{RT^2}p \tag{3.20}$$

$$\frac{\mathrm{d}L}{\mathrm{d}T}=c_p-c_p'+\frac{L}{T}-\left(\frac{\partial v}{\partial T}-\frac{\partial v'}{\partial T}\right)\frac{L}{v-v'}\approx c_p-c_p' \tag{3.21}$$

$$\ln p=\int_{T_0}^{T}\frac{\mathrm{d}T}{RT^2}\int_{T_0}^{T}(c_p-c_p')\mathrm{d}T-\frac{L_0}{RT}+C_0 \tag{3.22}$$

$$\ln p=A-\frac{B}{T}+C\ln T \tag{3.23}$$

3.4 曲面分界平衡和液滴形成

1. 曲面分界平衡条件:

$$\begin{cases}\delta F^\alpha=-p^\alpha\delta V^\alpha+\mu^\alpha\delta n^\alpha\\ \delta F^\beta=-p^\beta\delta V^\beta+\mu^\beta\delta n^\beta\\ \delta F^\gamma=\sigma\delta A\end{cases} \tag{3.24}$$

$$\delta F=-\left(p^\alpha-p^\beta-\frac{2\sigma}{r}\right)\delta V^\alpha+(\mu^\alpha-\mu^\beta)\delta n^\alpha=0 \tag{3.25}$$

$$p^\alpha=p^\beta+\frac{2\sigma}{r},\quad \mu^\alpha(p^\alpha,T)=\mu^\beta(p^\beta,T) \tag{3.26}$$

2. 平面和曲面分界面的平衡条件:

$$\mu^\alpha(p,T)=\mu^\beta(p,T),\quad \mu^\alpha\left(p'+\frac{2\sigma}{r},T\right)=\mu^\beta(p',T) \tag{3.27}$$

3. 液滴化学势:按压强展开

$$\mu^\alpha\left(p'+\frac{2\sigma}{r},T\right)=\mu^\alpha(p,T)+\left(p'-p+\frac{2\sigma}{r}\right)v^\alpha \tag{3.28}$$

4. 蒸汽化学势:看作理想气体

$$\mu^\beta(p',T)=\mu^\beta(p,T)+RT\ln\frac{p'}{p} \tag{3.29}$$

5. 形成液滴需要的蒸汽压:

$$p'-p\ll\frac{2\sigma}{r}\Rightarrow\ln\frac{p'}{p}=\frac{2\sigma v^\alpha}{RTr} \tag{3.30}$$

6. 临界半径:

$$r_c=\frac{2\sigma v^\alpha}{RT\ln\frac{p'}{p}} \tag{3.31}$$

3.5 相变分类

1. Van der Waals 气体的气-液相变:
   (1) Maxwell 等面积法则
   (2) 临界点:

$$\left(\frac{\partial p}{\partial v}\right)_T=0,\quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T=0 \tag{3.32}$$

$$v_c=3b,\quad p_c=\frac{a}{27b^2},\quad T_c=\frac{8a}{27Rb},\quad \frac{RT_c}{p_cV_{mc}}=\frac{8}{3}=2.667 \tag{3.33}$$

   (3) Van der Waals 对比方程:

$$\left(\widetilde{p}+\frac{3}{\widetilde{v}^2}\right)(3\widetilde{v}-1)=8\widetilde{T},\quad \widetilde{T}=\frac{T}{T_c},\quad \widetilde{p}=\frac{p}{p_c},\quad \widetilde{v}=\frac{v}{v_c} \tag{3.34}$$

2. 相变分类：

(1) 一级相变：相变点 μ 连续，μ 一级偏微商不连续

$$\left(\frac{\partial\mu}{\partial T}\right)_p = -s, \quad \left(\frac{\partial\mu}{\partial p}\right)_T = v \tag{3.35}$$

(2) 二级相变：相变点 μ 和 μ 一级偏微商连续，μ 二级偏微商不连续或发散

$$\left(\frac{\partial^2\mu}{\partial T^2}\right) = -\frac{c_p}{T}, \quad \left(\frac{\partial^2\mu}{\partial T^2}\right) = -v\kappa_T, \quad \frac{\partial^2\mu}{\partial T\partial p} = v\alpha \tag{3.36}$$

(3) n 级相变：相变点 μ 和 μ 直到 $(n-1)$ 级的偏微商连续，μ 的 n 级偏微商连续

3. 相变特点：

(1) 一级相变：相变点有两相共存和亚稳态，宏观状态发生突变

(2) 二级相变：相变点无两相共存和亚稳态，宏观状态不发生突变，对称性自发破缺

4. Ehrenfest 方程：

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{c_p^\beta - c_p^\alpha}{Tv(\alpha^\beta - \alpha^\alpha)} = \frac{\alpha^\beta - \alpha^\alpha}{\kappa_T^\beta - \kappa_T^\alpha} \tag{3.37}$$

3.6 临界现象和临界指数

1. 临界指数：

$$f(t) = At^\lambda(1 + Bt^\lambda + \cdots) \xrightarrow{t\to 0} t^\lambda, \quad t = \frac{T - T_c}{T_c} \tag{3.38}$$

2. 气-液相变的临界指数：

$$\rho_l - \rho_g \sim (-t)^\beta, \quad t \to 0^-, \quad p = p_c \tag{3.39}$$

$$|p - p_c| \sim |\rho - \rho_c|^\delta, \quad t = 0, \quad p \to p_c \tag{3.40}$$

$$\kappa_T \sim |t|^{-\gamma}, \quad t \to 0, \quad p = p_c \tag{3.41}$$

$$C_V \sim |t|^{-\alpha}, \quad t \to 0, \quad p = p_c \tag{3.42}$$

3. 顺磁-铁磁相变的临界指数：

$$\mathscr{M} \sim (-t)^\beta, \quad t \to 0^-, \quad \mathscr{H} = 0 \tag{3.43}$$

$$|\mathscr{H}| \sim |\mathscr{M}|^\delta, \quad t = 0, \quad \mathscr{H} \to 0 \tag{3.44}$$

$$\chi_m^0 \sim |t|^{-\gamma}, \quad t \to 0, \quad \mathscr{H} = 0 \tag{3.45}$$

$$C_{\mathscr{H}}^0 \sim |t|^{-\alpha}, \quad t \to 0, \quad \mathscr{H} = 0 \tag{3.46}$$

4. 临界指数标度律：

$$\alpha + 2\beta + \gamma \approx 2, \quad \beta(\delta - 1) \approx \gamma \tag{3.47}$$

3.7 Landau 连续相变理论

1. 序参量：高温无序相值为 0，低温有序相值不为 0
2. 对称性破缺：无序相空间各向同性，有序相对称性破缺
3. Landau 理论的临界指数：

(1) 临界指数 $\beta = \frac{1}{2}$：

$$F(T, \mathscr{M}) = a_0(T) + a_2(T - T_c)\mathscr{M}^2 + a_4\mathscr{M}^4, \quad T \to T_c, \quad \mathscr{H} = 0 \tag{3.48}$$

$$\left(\frac{\partial F}{\partial \mathscr{M}}\right)_T = 0, \quad \left(\frac{\partial^2 F}{\partial \mathscr{M}^2}\right)_T > 0 \Rightarrow \mathscr{M} = \begin{cases} 0 & T \to T_c^+ \\ \pm\sqrt{\dfrac{a_2(T_c - T)}{2a_4}} & T \to T_c^- \end{cases} \tag{3.49}$$

(2) 临界指数 $\delta = 3$：

$$G(T,\mathscr{H}) = F(T,\mathscr{M}) - \mu_0\mathscr{M}\mathscr{H} = a_0(T) - \mu_0\mathscr{H}\mathscr{M} + a_2(T-T_c)\mathscr{M}^2 + a_4\mathscr{M}^4, \quad \mathscr{H}\to 0 \tag{3.50}$$

$$\left(\frac{\partial G}{\partial \mathscr{M}}\right)_{T,\mathscr{H}} = 0 \Rightarrow \mu_0\mathscr{H} = 2a_2(T-T_c)\mathscr{M} + 4a_4\mathscr{M}^3 \xrightarrow{T=T_c} 4a_4\mathscr{M}^3 \tag{3.51}$$

(3) 临界指数 $\gamma = 1$：

$$\chi_m^0 = \left(\frac{\partial \mathscr{M}}{\partial \mathscr{H}}\right)_T = \frac{\mu_0}{2a_2(T-T_c)+12a_4\mathscr{M}^2} = \begin{cases} \dfrac{\mu_0}{2a_2}(T-T_c)^{-1} & T\to T_c^+ \\ \dfrac{\mu_0}{4a_2}(T_c-T)^{-1} & T\to T_c^- \end{cases}, \quad \mathscr{H}=0 \tag{3.52}$$

(4) 临界指数 $\alpha = 0$：

$$S = -\left(\frac{\partial F}{\partial T}\right)_{\mathscr{M}} = S_0(T) - a_2\mathscr{M}^2 = \begin{cases} S_0(T) & T\to T_c^+ \\ S_0(T) - \dfrac{a_2}{2a_4}(T_c-T) & T\to T_c^- \end{cases} \tag{3.53}$$

$$C_{\mathscr{H}} = T\left(\frac{\partial S}{\partial T}\right)_{\mathscr{H}} = \begin{cases} C_{\mathscr{M}}^0 & T\to T_c^+ \\ C_{\mathscr{M}}^0 + \dfrac{a_2^2}{2a_4}T_c & T\to T_c^- \end{cases} \tag{3.54}$$

4. 普适性假设：空间维数 d 和序参量维数 n 决定临界现象和临界指数
5. Landau 理论是平均场理论，忽略了涨落，部分情况下失效
6. Ginzburg 判据：Landau 理论适用条件

$$\left(\frac{\xi}{\xi_0}\right)^{d-4} = |t|^{\frac{4-d}{2}} > \frac{A_d}{2\Delta c_v \xi_0^d} \Longleftrightarrow t \gg t_G = \left(\frac{A_d}{2\Delta c_v \xi_0^d}\right)^{\frac{2}{4-d}} \tag{3.55}$$

(1) 当 $d > 4$ 时，上式在临界点邻域恒成立，平均场理论适用
(2) 当 $d < 4$ 时，只有 t 足够大，平均场理论才适用

4 多元系的复相平衡和化学平衡

4.1 多元均匀系的热力学函数和基本方程

1. 热力学基本函数用偏摩尔量表达:

$$V = \sum_i n_i v_i, \quad U = \sum_i n_i u_i, \quad S = \sum_i n_i s_i \tag{4.1}$$

$$v_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j}, \quad u_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,p,n_j}, \quad s_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_j} \tag{4.2}$$

2. Gibbs 函数用偏摩尔量表达:

$$G = \sum_i n_i \mu_i, \quad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j} \tag{4.3}$$

3. 多元均匀系的热力学基本方程:

$$\mathrm{d}U(S,V,n_i) = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i \tag{4.4}$$

$$\mathrm{d}H(S,p,n_i) = T\mathrm{d}S + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i \tag{4.5}$$

$$\mathrm{d}F(T,V,n_i) = -S\mathrm{d}T - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i \tag{4.6}$$

$$\mathrm{d}G(T,p,n_i) = -S\mathrm{d}T + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i \tag{4.7}$$

4. Gibbs-Duhem 关系:

$$S\mathrm{d}T - V\mathrm{d}p + \sum_i n_i \mathrm{d}\mu_i = 0 \tag{4.8}$$

4.2 多元系的复相平衡

1. 多元系的复相平衡条件:

$$T^\alpha = T^\beta, \quad p^\alpha = p^\beta, \quad \mu^\alpha = \mu^\beta \tag{4.9}$$

2. Gibbs 相律:

$$f = k + 2 - \sigma \tag{4.10}$$

4.3 多元系的化学平衡

1. 化学反应方程:

$$\sum_i \nu_i A_i = 0 \tag{4.11}$$

2. Dalton 定律:

$$\mathrm{d}n_i = \nu_i \mathrm{d}n \tag{4.12}$$

3. 反应热:

$$Q_p = \Delta H = \mathrm{d}n \sum_i \nu_i h_i \tag{4.13}$$

4. 多元系的化学平衡条件:

$$\sum_i \nu_i \mu_i = 0 \tag{4.14}$$

4.4 混合理想气体

1. 混合理想气体的热力学函数：

$$pV = \sum_i n_i RT, \quad p = \sum_i p_i \tag{4.15}$$

$$G = \sum_i n_i \mu_i = \sum_i n_i RT(\varphi_i(T) + \ln(x_i p)) \tag{4.16}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{T,n_i} = \sum_i n_i \left(\int c_{pi} \frac{\mathrm{d}T}{T} - R\ln(x_i p) + s_{0i}\right) \tag{4.17}$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_{T,n_i} = \sum_i n_i \left(\int c_{pi} \mathrm{d}T + h_{0i}\right) \tag{4.18}$$

$$U = G - T\left(\frac{\partial G}{\partial T}\right)_{T,n_i} - p\left(\frac{\partial G}{\partial p}\right)_{T,n_i} = \sum_i n_i \left(\int c_{vi} \mathrm{d}T + u_{0i}\right) \tag{4.19}$$

2. 质量作用定律：

$$\prod_i p_i^{\nu_i} = K_p(T), \quad \ln K_p(T) = -\sum_i \nu_i \varphi_i(T) \tag{4.20}$$

$$\prod_i x_i^{\nu_i} = K(p,T), \quad K(p,T) = p^{-\nu} K_p(T) \tag{4.21}$$

3. 化学反应正向进行的条件：

$$\sum_i \nu_i \mu_i < 0 \Rightarrow \prod_i p_i^{\nu_i} < K_p(T) \tag{4.22}$$

4.5 热力学第三定律

1. 热力学第三定律：不可能通过有限手段使物体达到绝对零度
2. Nernst 定理：系统的熵在等温过程中的改变随热力学温度趋近于 0

$$\lim_{T\to 0} (\Delta S)_T = 0 \tag{4.23}$$

3. Nernst 定理的推论：

(1) 系统的热容：

$$\lim_{T\to 0} C_y = 0, \quad C_y = T\left(\frac{\partial S}{\partial T}\right)_y = \left(\frac{\partial S}{\partial \ln T}\right)_y \tag{4.24}$$

(2) 膨胀系数和压强系数：

$$\lim_{T\to 0} \alpha = 0, \quad \lim_{T\to 0} \beta = 0 \tag{4.25}$$

(3) 一级相变平衡曲线的斜率：

$$\lim_{T\to 0} \frac{\mathrm{d}p}{\mathrm{d}T} = \lim_{T\to 0} \frac{s^\beta - s^\alpha}{v^\beta - v^\alpha} = 0 \tag{4.26}$$

4. 绝对熵：

$$S(T,y) = \int_0^T \frac{C_y}{T} \mathrm{d}T, \quad S_0 = 0 \tag{4.27}$$

5 非平衡态热力学

5.1 熵平衡方程

1. 局域平衡近似下的热力学第二定律：

$$\mathrm{d}S = \mathrm{d}_e S + \mathrm{d}_i S, \quad \mathrm{d}_e S = \frac{\text{đ}Q}{T_e}, \quad \mathrm{d}_i S > 0 \tag{5.1}$$

2. 熵平衡方程：

$$\frac{\partial s}{\partial t} = \frac{\partial_e s}{\partial t} + \frac{\partial_i s}{\partial t} = -\nabla\cdot\boldsymbol{J}_s + \Theta \tag{5.2}$$

3. 输运过程的规律：
   (1) 热传导的 Fourier 定律：

$$\boldsymbol{J}_q = -\kappa\nabla T \tag{5.3}$$

   (2) 扩散的 Fick 定律：

$$\boldsymbol{J}_n = D_n\nabla n \tag{5.4}$$

   (3) 电流的 Ohm 定律：

$$\boldsymbol{J}_e = -\sigma\nabla\varphi \tag{5.5}$$

4. 线性唯象律：

$$J_k = \sum_l L_{kl}X_l \tag{5.6}$$

5. Onsager 关系：

$$L_{kl} = L_{lk} \tag{5.7}$$

6. Casimir 条件：

$$\Theta = \sum_k J_k X_k = \sum_{kl} L_{kl}X_k X_l \geqslant 0 \tag{5.8}$$

7. 最小熵产生定理：非平衡定态熵产生率最小

5.2 热传导

1. 热传导：
   (1) 能量守恒：

$$\frac{\partial u}{\partial t} + \nabla\cdot\boldsymbol{J}_u = 0, \quad \boldsymbol{J}_u = \boldsymbol{J}_q \tag{5.9}$$

   (2) 熵平衡方程：

$$\frac{\partial s}{\partial t} = \frac{1}{T}\frac{\partial u}{\partial t} = -\frac{1}{T}\nabla\cdot\boldsymbol{J}_q = -\nabla\cdot\frac{\boldsymbol{J}_q}{T} + \boldsymbol{J}_q\cdot\nabla\frac{1}{T} \tag{5.10}$$

$$\boldsymbol{J}_s = \frac{\boldsymbol{J}_q}{T}, \quad \Theta = \boldsymbol{J}_q\cdot\nabla\frac{1}{T} = \boldsymbol{J}_q\cdot\boldsymbol{X}_q \tag{5.11}$$

2. 热传导和输运过程：
   (1) 能量守恒：

$$\frac{\partial u}{\partial t} + \nabla\cdot\boldsymbol{J}_u = 0, \quad \boldsymbol{J}_u = \boldsymbol{J}_q + \mu\boldsymbol{J}_n \tag{5.12}$$

   (2) 熵平衡方程：

$$\frac{\partial s}{\partial t} = \frac{1}{T}\frac{\partial u}{\partial t} - \frac{\mu}{T}\frac{\partial n}{\partial t} = -\nabla\cdot\left(\frac{\boldsymbol{J}_q}{T}\right) + \boldsymbol{J}_q\cdot\nabla\frac{1}{T} - \frac{\boldsymbol{J}_n}{T}\cdot\nabla\mu \tag{5.13}$$

$$\boldsymbol{J}_s = \frac{\boldsymbol{J}_q}{T}, \quad \Theta = \boldsymbol{J}_q\cdot\nabla\frac{1}{T} - \frac{\boldsymbol{J}_n}{T}\cdot\nabla\mu = \boldsymbol{J}_q\cdot\boldsymbol{X}_q + \boldsymbol{J}_n\cdot\boldsymbol{X}_n \tag{5.14}$$

6 近独立子系的最概然分布

6.1 分布和微观态

1. 分布的约束条件：

$$\sum_l a_l = N, \quad \sum_l a_l \varepsilon_l = E \tag{6.1}$$

2. 微观态数目：

$$\varOmega_{M.B.}(a_l) = \frac{N!}{\prod_l a_l!}\prod_l \omega_l^{a_l}, \quad \varOmega_{B.E.}(a_l) = \prod_l \frac{(\omega_l + a_l - 1)!}{a_l!(\omega_l - 1)!}, \quad \varOmega_{F.D.}(a_l) = \prod_l \frac{\omega_l!}{a_l!(\omega_l - a_l)!} \tag{6.2}$$

非简并条件：

$$\frac{a_l}{\omega_l} \ll 1 \Rightarrow \varOmega_{B.E.} = \varOmega_{F.D.} = \frac{\varOmega_{M.B.}}{N!} \tag{6.3}$$

3. 最概然分布法：

$$\delta \ln \varOmega(a_l) = 0, \quad \delta N = 0, \quad \delta E = 0 \tag{6.4}$$

6.2 Boltzmann 分布

1. Maxwell-Boltzmann 分布：

$$\ln \varOmega_{M.B.} = N(\ln N - 1) - \sum_l a_l(\ln a_l - 1) + \sum_l a_l \ln \omega_l = N \ln N - \sum_l a_l \ln\left(\frac{a_l}{\omega_l}\right) \tag{6.5}$$

$$\delta \ln \varOmega_{M.B.} - \alpha\delta N - \beta\delta E = -\sum_l \left(\ln\frac{a_l}{\omega_l} + \alpha + \beta\varepsilon_l\right)\delta a_l = 0 \tag{6.6}$$

$$\widetilde{a}_l = \omega_l \mathrm{e}^{-\alpha-\beta\varepsilon_l} \tag{6.7}$$

2. MB 分布是尖锐成峰的极大：

$$\ln \varOmega_{M.B.}(\widetilde{a}_l + \delta a_l) = \ln \varOmega_{M.B.}(\widetilde{a}_l) + \frac{1}{2}\delta^2 \ln \varOmega_{M.B.}(\widetilde{a}_l) = \ln \varOmega_{M.B.}(\widetilde{a}_l) - \frac{1}{2}\sum_l \frac{(\delta a_l)^2}{\widetilde{a}_l} \tag{6.8}$$

$$\frac{\varOmega_{M.B.}(\widetilde{a}_l + \delta a_l)}{\varOmega_{M.B.}(\widetilde{a}_l)} = \exp\left[-\frac{1}{2}\sum_l \left(\frac{\delta a_l}{\widetilde{a}_l}\right)^2 \widetilde{a}_l\right] \tag{6.9}$$

3. MB 分布参数 α 和 β 的确定：

$$\sum_l \omega_l \mathrm{e}^{-\alpha-\beta\varepsilon_l} = N, \quad \sum_l \varepsilon_l \omega_l \mathrm{e}^{-\alpha-\beta\varepsilon_l} = E \tag{6.10}$$

6.3 Bose 分布和 Fermi 分布

1. Bose-Einstein 分布：

$$\ln \varOmega_{B.E.} \approx \sum_l [(\omega_l + a_l)\ln(\omega_l + a_l) - a_l \ln a_l - \omega_l \ln \omega_l] \tag{6.11}$$

$$\delta \ln \varOmega_{B.E.} - \alpha\delta N - \beta\delta E = \sum_l \left(\ln\frac{\omega_l + a_l}{a_l} - \alpha - \beta\varepsilon_l\right)\delta a_l = 0 \tag{6.12}$$

$$\widetilde{a}_l = \frac{\omega_l}{\mathrm{e}^{\alpha+\beta\varepsilon_l} - 1} \tag{6.13}$$

2. BE 分布参数 α 和 β 的确定：

$$\sum_l \frac{\omega_l}{\mathrm{e}^{\alpha+\beta\varepsilon_l} - 1} = N, \quad \sum_l \frac{\varepsilon_l\omega_l}{\mathrm{e}^{\alpha+\beta\varepsilon_l} - 1} = E \tag{6.14}$$

3. Fermi-Dirac 分布:

$$\ln \Omega_{F.D.} = \sum_l [\omega_l \ln \omega_l - a_l \ln a_l - (\omega_l - a_l) \ln (\omega_l - a_l)] \tag{6.15}$$

$$\delta \ln \Omega_{F.D.} - \alpha \delta N - \beta \delta E = \sum_l \left(\ln \frac{\omega_l - a_l}{a_l} - \alpha - \beta \varepsilon_l \right) \delta a_l = 0 \tag{6.16}$$

$$\widetilde{a}_l = \frac{\omega_l}{\mathrm{e}^{\alpha + \beta \varepsilon_l} + 1} \tag{6.17}$$

4. FD 分布参数 α 和 β 的确定:

$$\sum_l \frac{\omega_l}{\mathrm{e}^{\alpha + \beta \varepsilon_l} - 1} = N, \quad \sum_l \frac{\varepsilon_l \omega_l}{\mathrm{e}^{\alpha + \beta \varepsilon_l} + 1} = E \tag{6.18}$$

6.4 三种分布的关系

1. 三种分布:

$$\widetilde{a}_l = \frac{\omega_l}{\mathrm{e}^{\alpha + \beta \varepsilon_l} + \eta}, \quad \eta = \begin{cases} +1 & \text{FD 分布} \\ 0 & \text{MB 分布} \\ -1 & \text{BE 分布} \end{cases} \tag{6.19}$$

2. 非简并条件:

$$\mathrm{e}^{\alpha} \gg 1 \Rightarrow \frac{a_l}{\omega_l} \ll 1 \tag{6.20}$$

7 Boltzmann 统计

7.1 Boltzmann 统计的热力学函数

1. 子系配分函数：

$$Z_1(\beta, y_i) = \sum_l \omega_l \mathrm{e}^{-\beta\varepsilon_l} \tag{7.1}$$

2. 粒子数：

$$N = \mathrm{e}^{-\alpha} \sum_l \omega_l \mathrm{e}^{-\beta\varepsilon_l} = \mathrm{e}^{-\alpha} Z_1 \tag{7.2}$$

3. 内能：

$$U = \mathrm{e}^{-\alpha} \sum_l \varepsilon_l \omega_l \mathrm{e}^{-\beta\varepsilon_l} = \frac{N}{Z_1}\left(-\frac{\partial}{\partial\beta}\sum_l \omega_l \mathrm{e}^{-\beta\varepsilon_l}\right) = -N\frac{\partial}{\partial\beta}\ln Z_1 \tag{7.3}$$

4. 广义力：

$$Y_i = \sum_l \frac{\partial\varepsilon_l}{\partial y_i} a_l = \frac{N}{Z_1}\left(-\frac{1}{\beta}\frac{\partial}{\partial y_i}\sum_l \omega_l \mathrm{e}^{-\beta\varepsilon_l}\right) = -\frac{N}{\beta}\frac{\partial}{\partial y_i}\ln Z_1 \tag{7.4}$$

5. 功和热量：

$$đW = \sum_i \sum_l \frac{\partial\varepsilon_l}{\partial y_i} a_l \mathrm{d}y_i = \sum_l a_l \mathrm{d}\varepsilon_l, \quad đQ = \sum_l \varepsilon_l \mathrm{d}a_l \tag{7.5}$$

6. 参数 β：

$$\frac{1}{T}(\mathrm{d}U - đW) = \mathrm{d}S, \quad \beta(\mathrm{d}U - đW) = N\mathrm{d}\left(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1\right) \Rightarrow \beta = \frac{1}{kT} \tag{7.6}$$

7. 熵：

$$S = Nk\left(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1\right) \tag{7.7}$$

$$S = k\left(N\ln N + \sum_l(\alpha + \beta\varepsilon_l)a_l\right) = k\ln\Omega_{M.B.} \tag{7.8}$$

8. 自由能：

$$F = -N\frac{\partial}{\partial\beta}\ln Z_1 - NkT\left(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1\right) = -NkT\ln Z_1 \tag{7.9}$$

7.2 单原子理想气体

1. 子系配分函数：

$$Z_1 = \frac{1}{h^3}\int \mathrm{d}^3r \int \mathrm{e}^{-\frac{\beta}{2m}p_x^2}\mathrm{d}p_x \int \mathrm{e}^{-\frac{\beta}{2m}p_y^2}\mathrm{d}p_y \int \mathrm{e}^{-\frac{\beta}{2m}p_z^2}\mathrm{d}p_z = V\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} \tag{7.10}$$

2. 压强：

$$p = \frac{N}{\beta}\frac{\partial}{\partial V}\ln Z_1 = \frac{N}{\beta V} = \frac{N}{V}kT \tag{7.11}$$

3. 内能：

$$U = -N\frac{\partial}{\partial\beta}\ln Z_1 = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT \tag{7.12}$$

4. 熵：不可分辨性导致 Gibbs 校正因子

$$S = Nk\left(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1\right) - k\ln N! = Nk\left(\ln\frac{V}{N} - 3\ln\lambda_T + \frac{5}{2}\right), \quad \lambda_T = \left(\frac{h^2}{2\pi mkT}\right)^{\frac{1}{2}} \tag{7.13}$$

5. 非简并条件：

$$\mathrm{e}^{\alpha} = \frac{Z_1}{N} = \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \frac{1}{n\lambda_T^3} \gg 1 \Rightarrow n\lambda_T^3 \ll 1 \tag{7.14}$$

7.3 Maxwell 速度分布

1. $\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$ 内的分子数:

$$\mathrm{d}N(p_x,p_y,p_z)=\mathrm{e}^{-\alpha-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)}\frac{V}{h^3}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \tag{7.15}$$

$$\frac{V}{h^3}\int \mathrm{e}^{-\alpha-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z=N\Rightarrow \mathrm{e}^{-\alpha}=\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}=n\lambda_T^{-3} \tag{7.16}$$

$$\mathrm{d}N(p_x,p_y,p_z)=N\left(\frac{1}{2\pi mkT}\right)^{\frac{3}{2}}\mathrm{e}^{-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \tag{7.17}$$

2. Maxwell 速度分布:

$$\mathrm{d}N(v_x,v_y,v_z)=N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\mathrm{e}^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \tag{7.18}$$

$$\frac{\mathrm{d}N(v_x,v_y,v_z)}{N}=f(v_x,v_y,v_z)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z=\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\mathrm{e}^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \tag{7.19}$$

3. Maxwell 速率分布:

$$\mathrm{d}N(v)=4\pi v^2N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\mathrm{e}^{-\frac{m}{2kT}v^2}\mathrm{d}v \tag{7.20}$$

$$\frac{\mathrm{d}N(v)}{N}=f(v)\mathrm{d}v=4\pi v^2\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\mathrm{e}^{-\frac{m}{2kT}v^2}\mathrm{d}v=4\pi v^2f(v_x,v_y,v_z)\mathrm{d}v \tag{7.21}$$

4. 三种速率:

(1) 平均速率:

$$\langle v\rangle=\int_0^{+\infty}vf(v)\mathrm{d}v=\sqrt{\frac{8kT}{\pi m}}=\sqrt{\frac{8RT}{\pi M}} \tag{7.22}$$

(2) 方均根速率:

$$v_s=\left(\int_0^{+\infty}v^2f(v)\mathrm{d}v\right)^{\frac{1}{2}}=\sqrt{\frac{3kT}{m}}=\sqrt{\frac{3RT}{M}} \tag{7.23}$$

(3) 最概然速率:

$$v_p=\sqrt{\frac{2kT}{m}}=\sqrt{\frac{2RT}{M}} \tag{7.24}$$

5. Maxwell 平动动能分布:

$$\mathrm{d}N(\varepsilon)=2\pi\varepsilon^{\frac{1}{2}}N\left(\frac{1}{\pi kT}\right)^{\frac{3}{2}}\mathrm{e}^{-\frac{\varepsilon}{kT}}\mathrm{d}\varepsilon \tag{7.25}$$

$$\frac{\mathrm{d}N(\varepsilon)}{N}=f(\varepsilon)\mathrm{d}\varepsilon=\frac{2}{\sqrt{\pi}}\left(\frac{1}{kT}\right)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}\mathrm{e}^{-\frac{\varepsilon}{kT}}\mathrm{d}\varepsilon \tag{7.26}$$

6. 平动动能:

(1) 平均平动动能:

$$\langle\varepsilon\rangle=\int_0^{+\infty}\varepsilon f(\varepsilon)\mathrm{d}\varepsilon=\frac{3}{2}kT \tag{7.27}$$

(2) 方均根平动动能:

$$\varepsilon_s=\left(\int_0^{+\infty}(\varepsilon)^2f(\varepsilon)\mathrm{d}\varepsilon\right)^{\frac{1}{2}}=\frac{\sqrt{15}}{2}kT \tag{7.28}$$

(3) 最概然平动动能:

$$\varepsilon_p=\frac{1}{2}kT \tag{7.29}$$

7. 气体分子碰壁数:

$$\varGamma=\frac{\mathrm{d}N}{\mathrm{d}A\mathrm{d}t}=\frac{1}{4}n\langle v\rangle \tag{7.30}$$

7.4 能均分定理

1. 能均分定理：系统微观能量表达式中每一独立平方项的平均值为 $\dfrac{1}{2}kT$

$$\varepsilon=\varepsilon_k+\varepsilon_p=\frac{1}{2}\sum_{i=1}^{n}a_i\xi_i^2+\varepsilon'(\xi_{n+1},\ldots,\xi_{2r}) \tag{7.31}$$

$$\left\langle\frac{1}{2}a_i\xi_i^2\right\rangle=\frac{1}{N}\int\frac{1}{2}a_i\xi_i^2\mathrm{e}^{-\alpha-\beta\varepsilon}\frac{\mathrm{d}\omega}{h^r}=0-\frac{1}{2\beta}\frac{1}{Z_1}\int\mathrm{e}^{-\beta\varepsilon}\frac{\mathrm{d}\omega}{h^r}=\frac{1}{2\beta}=\frac{1}{2}kT \tag{7.32}$$

2. 分子能量：

(1) 单原子气体分子：

$$\varepsilon=\frac{1}{2m}(p_x^2+p_y^2+p_z^2),\quad i=3 \tag{7.33}$$

(2) 双原子气体分子：

$$\varepsilon=\frac{1}{2m}(p_x^2+p_y^2+p_z^2)+\frac{1}{2I}\left(p_\theta^2+\frac{1}{\sin^2\theta}p_\varphi^2\right),\quad i=5 \tag{7.34}$$

(3) 多原子气体分子：

$$\varepsilon=\frac{1}{2m}(p_x^2+p_y^2+p_z^2)+\frac{1}{2I_A}p_A^2+\frac{1}{2I_B}p_B^2+\frac{1}{2I_C}p_C^2,\quad i=6 \tag{7.35}$$

(4) 一个自由度上的固体分子：

$$\varepsilon_\lambda=\frac{1}{2m}p^2+\frac{1}{2}m\omega^2q^2,\quad i=6 \tag{7.36}$$

3. 热容：

$$\langle\varepsilon\rangle=\frac{i}{2}kT,\quad U=N\langle\varepsilon\rangle=\frac{i}{2}NkT \tag{7.37}$$

$$C_V=\frac{i}{2}Nk,\quad C_p=C_V+Nk=\frac{i+2}{2}Nk,\quad \gamma=\frac{i+2}{i} \tag{7.38}$$

7.5 理想气体的热容

1. 理想气体的热容：

$$\varepsilon=\varepsilon^t+\varepsilon^r+\varepsilon^v+\varepsilon^e,\quad \omega=\omega^t\omega^r\omega^v\omega^e \tag{7.39}$$

$$Z_1=\sum_{trve}\omega^t\omega^r\omega^v\omega^e\mathrm{e}^{-\beta(\varepsilon^t+\varepsilon^r+\varepsilon^v+\varepsilon^e)}=Z_1^tZ_1^rZ_1^vZ_1^e \tag{7.40}$$

$$U=-N\frac{\partial}{\partial\beta}\ln Z_1=U^t+U^r+U^v+U^e \tag{7.41}$$

$$C_V=\frac{\mathrm{d}U}{\mathrm{d}T}=C_V^t+C_V^r+C_V^v+C_V^e \tag{7.42}$$

2. 电子部分：

$$Z_1^e=\sum_l\omega_l^e\mathrm{e}^{-\beta\varepsilon_l^e}\approx\omega_0^e\mathrm{e}^{-\beta\varepsilon_0^e} \tag{7.43}$$

$$U^e=-N\frac{\partial}{\partial\beta}\ln Z_1^e=N\varepsilon_0^e \tag{7.44}$$

$$C_V^e=0 \tag{7.45}$$

3. 平动部分：

$$Z_1^t=V\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} \tag{7.46}$$

$$U^t=-N\frac{\partial}{\partial\beta}\ln Z_1^t=\frac{3N}{2\beta}=\frac{3}{2}NkT \tag{7.47}$$

$$C_V^t=\frac{3}{2}Nk \tag{7.48}$$

4. 转动部分：

$$\varepsilon_l^r=\frac{\hbar^2}{2I}l(l+1),\quad \omega_l^r=2l+1,\quad k\theta_r=\frac{\hbar^2}{2I},\quad x_r=\frac{\theta_r}{T} \tag{7.49}$$

(1) 异核双原子：

$$Z_1^r=\sum_{l=0}^{+\infty}(2l+1)\mathrm{e}^{-l(l+1)x_r}=2\mathrm{e}^{\frac{1}{4}x_r}\sum_{l=0}^{+\infty}\left(l+\frac{1}{2}\right)\mathrm{e}^{-\left(l+\frac{1}{2}\right)^2x_r}=\mathrm{e}^{\frac{1}{4}x_r}\left(\frac{1}{x_r}+\frac{1}{12}\right) \tag{7.50}$$

$$U^r=-N\frac{\partial}{\partial\beta}\ln Z_1^r=\left(\frac{12}{12+x_r}-\frac{1}{4}x_r\right)NkT\approx\begin{cases}NkT & x_r\to 0\\ -\frac{1}{4}Nk\theta_r & x_r\to+\infty\end{cases} \tag{7.51}$$

$$C_V^r=\frac{\frac{1}{6}x_r+1}{\left(\frac{1}{12}x_r+1\right)^2}Nk\approx\begin{cases}Nk & x_r\to 0\\ 24Nkx_r^{-1}\to 0 & x_r\to+\infty\end{cases} \tag{7.52}$$

(2) 同核双原子：以正氢和仲氢为例

$$Z_1^r=\frac{3}{4}Z_{1o}^r+\frac{1}{4}Z_{1p}^r \tag{7.53}$$

$$Z_{1o}^r=\sum_{l=1,3,5,\dots}^{+\infty}(2l+1)\mathrm{e}^{-l(l+1)x_r},\quad Z_{1p}^r=\sum_{l=0,2,4,\dots}^{+\infty}(2l+1)\mathrm{e}^{-l(l+1)x_r} \tag{7.54}$$

5. 振动部分：

$$\varepsilon_l^v=\left(l+\frac{1}{2}\right)\hbar\omega,\quad \omega_l^v=1,\quad k\theta_v=\hbar\omega,\quad x_v=\frac{\theta_v}{T} \tag{7.55}$$

$$Z_1^v=\sum_{l=0}^{+\infty}\mathrm{e}^{-\left(l+\frac{1}{2}\right)x_v}=\frac{\mathrm{e}^{-\frac{1}{2}x_v}}{1-\mathrm{e}^{-x_v}} \tag{7.56}$$

$$U^v=-N\frac{\partial}{\partial\beta}\ln Z_1^v=\frac{1}{2}Nk\theta_v+\frac{Nk\theta_v}{\mathrm{e}^{x_v}-1}\approx\begin{cases}NkT & x_v\to 0\\ \frac{1}{2}Nk\theta_v & x_v\to+\infty\end{cases} \tag{7.57}$$

$$C_V^v=Nkx_v^2\frac{\mathrm{e}^{x_v}}{(\mathrm{e}^{x_v}-1)^2}\approx\begin{cases}Nk & x_v\to 0\\ Nkx_v^2\mathrm{e}^{-x_v}\to 0 & x_v\to+\infty\end{cases} \tag{7.58}$$

7.6 顺磁性固体

1. 子系配分函数：

$$Z_1=\mathrm{e}^{\beta\mu_BB}+\mathrm{e}^{-\beta\mu_BB}=2\cosh x_B,\quad x_B=\frac{\mu_BB}{kT} \tag{7.59}$$

2. 磁矩：

$$m=\frac{N}{\beta}\frac{\partial}{\partial B}\ln Z_1=N\mu_B\tanh x_B\approx\begin{cases}\dfrac{N\mu_B^2}{kT}B=\chi\mathscr{H} & x_B\to 0\\ N\mu_B & x_B\to+\infty\end{cases} \tag{7.60}$$

3. 内能：

$$U=-N\frac{\partial}{\partial\beta}\ln Z_1=-N\mu_BB\tanh x_B=-mB \tag{7.61}$$

4. 热容：

$$C_{\mathscr{H}}=\left(\frac{\partial U}{\partial T}\right)_{\mathscr{H}}=Nk\frac{x_B^2}{\cosh^2x_B}\approx\begin{cases}Nkx_B^2\to 0 & x_B\to 0\\ Nk(2x_B)^2\mathrm{e}^{-2x_B}\to 0 & x\to+\infty\end{cases} \tag{7.62}$$

5. 熵：

$$S=Nk\left(\ln Z_1-\beta\frac{\partial}{\partial\beta}\ln Z_1\right)\approx Nk(\ln 2+\ln\cosh x_B-x_B\tanh x_B)\approx\begin{cases}Nk\ln 2 & x_B\to 0\\ 0 & x_B\to+\infty\end{cases} \tag{7.63}$$

7.7 负温状态

1. 两能级粒子数:

$$N = N_+ + N_-, \quad E = N_+\varepsilon - N_-\varepsilon \tag{7.64}$$

$$N_+ = \frac{1}{2}\left(1+\frac{E}{\varepsilon}\right), \quad N_- = \frac{1}{2}\left(1-\frac{E}{\varepsilon}\right) \tag{7.65}$$

2. 熵:

$$\begin{aligned} S &= k\ln\frac{N!}{N_+!N_-!} = k(N\ln N - N_+\ln N_+ - N_-\ln N_-) \\ &= Nk\left[\ln 2 - \frac{1}{2}\left(1+\frac{E}{N\varepsilon}\right)\ln\left(1+\frac{E}{N\varepsilon}\right) - \frac{1}{2}\left(1-\frac{E}{N\varepsilon}\right)\ln\left(1-\frac{E}{N\varepsilon}\right)\right] \end{aligned} \tag{7.66}$$

3. 温度:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N = \frac{k}{2\varepsilon}\ln\frac{N\varepsilon - E}{N\varepsilon + E} = \frac{k}{2\varepsilon}\ln\frac{N_-}{N_+} \tag{7.67}$$

4. 系统达到负温状态的条件:
   (1) 粒子能级有上限
   (2) 负温系统达到平衡的弛豫时间远小于负温和正温系统达到平衡的弛豫时间

8 Bose 统计和 Fermi 统计

8.1 Bose 统计和 Fermi 统计的热力学函数

1. 巨配分函数:

$$\Xi(\alpha,\beta,y_i)=\prod_l\left(1\pm \mathrm{e}^{-\alpha-\beta\varepsilon_l}\right)^{\pm\omega_l} \tag{8.1}$$

2. 粒子数:

$$\langle N\rangle=\sum_l\frac{\omega_l}{\mathrm{e}^{\alpha+\beta\varepsilon_l}\pm 1}=-\frac{\partial}{\partial\alpha}\ln\Xi \tag{8.2}$$

3. 内能:

$$U=\sum\frac{\omega_l\varepsilon_l}{\mathrm{e}^{\alpha+\beta\varepsilon_l}\pm 1}=-\frac{\partial}{\partial\beta}\ln\Xi \tag{8.3}$$

4. 广义力:

$$Y_i=\sum_l\frac{\partial\varepsilon_l}{\partial y_i}\frac{\omega_l}{\mathrm{e}^{\alpha+\beta\varepsilon_l}\pm 1}=-\frac{1}{\beta}\frac{\partial}{\partial y_i}\ln\Xi \tag{8.4}$$

5. 参数 α, β:

$$\frac{1}{T}(\mathrm{d}U-đW-\mu\mathrm{d}\langle N\rangle)=\mathrm{d}S,\quad \beta\left(\mathrm{d}U-đW+\frac{\alpha}{\beta}\mathrm{d}\langle N\rangle\right)=\mathrm{d}\left(\ln\Xi-\alpha\frac{\partial}{\partial\alpha}\ln\Xi-\beta\frac{\partial}{\partial\beta}\ln\Xi\right) \tag{8.5}$$

$$\Rightarrow\beta=\frac{1}{kT},\quad \alpha=-\frac{\mu}{kT} \tag{8.6}$$

6. 熵:

$$S=k\left(\ln\Xi-\alpha\frac{\partial}{\partial\alpha}\ln\Xi-\beta\frac{\partial}{\partial\beta}\ln\Xi\right)=k(\ln\Xi+\alpha\langle N\rangle+\beta U) \tag{8.7}$$

$$S=k\ln\Omega,\quad \Omega=\Omega_{B.E.}\ \text{or}\ \Omega_{F.D.} \tag{8.8}$$

7. 巨热力势:

$$J=U-kT(\ln\Xi+\alpha\langle N\rangle+\beta U)-\alpha kT\langle N\rangle=-kT\ln\Xi \tag{8.9}$$

8.2 弱简并理想气体

1. 巨配分函数:

$$\begin{aligned}\ln\Xi&=-\int\frac{\mathrm{d}\omega}{h^3}\ln\left(1-\mathrm{e}^{-\alpha-\beta\varepsilon}\right)=-\frac{2\pi V}{h^3}\left(\frac{2m}{\beta}\right)^{\frac{3}{2}}\int_0^{+\infty}\ln\left(1-\mathrm{e}^{-\alpha-x}\right)x^{\frac{1}{2}}\mathrm{d}x\\&=-\frac{2\pi V}{h^3}\left(\frac{2m}{\beta}\right)^{\frac{3}{2}}\int_0^{+\infty}\left(-\sum_{\lambda=1}^{+\infty}\frac{\mathrm{e}^{-\lambda(\alpha+x)}}{\lambda}\right)x^{\frac{1}{2}}\mathrm{d}x=\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}\sum_{\lambda=1}^{+\infty}\frac{\mathrm{e}^{-\lambda\alpha}}{\lambda^{\frac{5}{2}}}=\frac{V}{\lambda_T^3}g_{\frac{5}{2}}(z)\end{aligned} \tag{8.10}$$

$$x=\beta\varepsilon,\quad z=e^{-\alpha},\quad \lambda_T=\left(\frac{h^2}{2\pi mkT}\right)^{\frac{1}{2}},\quad g_m(z)=\sum_{\lambda=1}^{+\infty}\frac{z^\lambda}{\lambda^m},\quad z\frac{\mathrm{d}g_m(z)}{\mathrm{d}z}=g_{m-1}(z) \tag{8.11}$$

2. 粒子数:

$$N=-\frac{\partial}{\partial\alpha}\ln\Xi=\frac{V}{\lambda_T^3}g_{\frac{3}{2}}(z) \tag{8.12}$$

3. 压强:

$$p=\frac{1}{\beta}\frac{\partial}{\partial V}\ln\Xi=\frac{1}{\beta\lambda_T^3}g_{\frac{5}{2}}(z) \tag{8.13}$$

4. 内能:

$$U=-\frac{\partial}{\partial\beta}\ln\Xi=\frac{3}{2}kT\frac{V}{\lambda_T^3}g_{\frac{5}{2}}(z) \tag{8.14}$$

5. 熵:

$$S=k(\ln\Xi+\alpha N+\beta U)=k\frac{V}{\lambda_T^3}\left(\frac{5}{2}g_{\frac{5}{2}}(z)+\alpha g_{\frac{3}{2}}(z)\right) \tag{8.15}$$

6. 弱简并条件:

$$\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} \approx \frac{z+2^{-\frac{5}{2}}z^2}{z+2^{-\frac{3}{2}}z^2} \approx 1-2^{-\frac{5}{2}}z \tag{8.16}$$

7. 弱简并理想气体:

$$p = nkT\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} \approx nkT(1 \pm 2^{-\frac{5}{2}}z) \tag{8.17}$$

$$U = \frac{3}{2}NkT\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} \approx \frac{3}{2}NkT(1 \pm 2^{-\frac{5}{2}}z) \tag{8.18}$$

$$S = Nk\left(\alpha + \frac{5}{2}\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)}\right) \approx Nk\left(\alpha + \frac{5}{2} \pm 5\cdot 2^{-\frac{7}{2}}z\right) \tag{8.19}$$

8.3 光子气体

1. 光子气体的 Bose 分布:

$$a_l = \frac{\omega_l}{\mathrm{e}^{\beta\varepsilon_l}-1}, \quad \alpha = 0, \quad \mu = 0 \tag{8.20}$$

2. 态密度:

$$D(\omega)\mathrm{d}\omega = 2\frac{V}{h^3}4\pi p^2\mathrm{d}p = \frac{V}{\pi^2c^3}\omega^2\mathrm{d}\omega \tag{8.21}$$

3. 内能:

$$U(\omega,T)\mathrm{d}\omega = \hbar\omega\frac{D(\omega)\mathrm{d}\omega}{\mathrm{e}^{\beta\hbar\omega}-1} = \frac{V}{\pi^2c^3}\frac{\hbar\omega^3}{\mathrm{e}^{\frac{\hbar\omega}{kT}}-1}\mathrm{d}\omega, \quad x = \frac{\hbar\omega}{kT} \tag{8.22}$$

$$U(\omega,T)\mathrm{d}\omega \to \frac{V}{\pi^2c^3}\omega^2kT\mathrm{d}\omega, \quad x \to 0 \tag{8.23}$$

$$U(\omega,T)\mathrm{d}\omega \to \frac{V}{\pi^2c^3}\hbar\omega^3\mathrm{e}^{-\frac{\hbar\omega}{kT}}\mathrm{d}\omega, \quad x \to +\infty \tag{8.24}$$

$$U(T) = \frac{V}{\pi^2c^3}\int_0^{+\infty}\frac{\hbar\omega^3}{\mathrm{e}^{\frac{\hbar\omega}{kT}}-1}\mathrm{d}\omega = \frac{V\hbar}{\pi^2c^3}\left(\frac{kT}{\hbar}\right)^4\int_0^{+\infty}\frac{x^3}{\mathrm{e}^x-1}\mathrm{d}x = \frac{\pi^2k^4}{15c^3\hbar^3}VT^4 \tag{8.25}$$

4. Wein 位移定律:

$$\frac{\partial}{\partial\omega}U(\omega,T) = 0 \Rightarrow x_m = 2.822 \tag{8.26}$$

$$\frac{\partial}{\partial\lambda}U(\lambda,T) = 0 \Rightarrow \lambda_mT = b \tag{8.27}$$

5. 巨配分函数:

$$\begin{aligned}\ln\varXi &= -\int_0^{+\infty}D(\omega)\mathrm{d}\omega\ln\left(1-\mathrm{e}^{-\alpha-\beta\varepsilon}\right) = -\frac{V}{\pi^2c^3}\frac{1}{(\beta\hbar)^3}\int_0^{+\infty}x^2\ln(1-\mathrm{e}^{-x})\mathrm{d}x \\ &= -\frac{V}{\pi^2c^3}\frac{1}{(\beta\hbar)^3}\left(0-\frac{1}{3}\int_0^{+\infty}\frac{x^3}{\mathrm{e}^x-1}\mathrm{d}x\right) = \frac{\pi^2V}{45c^3}\frac{1}{(\beta\hbar)^3}\end{aligned} \tag{8.28}$$

6. 压强:

$$p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln\varXi = \frac{\pi^2k^4}{45c^3\hbar^3}T^4 = \frac{1}{3}u \tag{8.29}$$

7. 内能:

$$U = -\frac{\partial}{\partial\beta}\ln\varXi = \frac{\pi^2k^4}{15c^3\hbar^3}VT^4 \tag{8.30}$$

8. 熵:

$$S = k(\ln\varXi + \beta U) = \frac{4}{45}\frac{\pi^2k^4}{c^3\hbar^3}VT^3 \tag{8.31}$$

8.4 理想 Bose 气体的 Bose-Einstein 凝聚

1. 化学势:

$$a_l = \frac{\omega_l}{e^{\frac{\varepsilon_l - \mu}{kT}} - 1} > 0 \Rightarrow \mu(T, n) < \varepsilon_0 = 0 \tag{8.32}$$

$$n = \frac{N}{V} = \frac{1}{V} \sum_l \frac{\omega_l}{e^{\frac{\varepsilon_l - \mu}{kT}} - 1} \to \frac{2\pi}{h^3} (2m)^{\frac{3}{2}} \int_0^{+\infty} \frac{\varepsilon^{\frac{1}{2}} d\varepsilon}{e^{\frac{\varepsilon - \mu}{kT}} - 1} \tag{8.33}$$

2. 临界温度:

$$n = \frac{N}{V} = \frac{2\pi}{h^3} (2m)^{\frac{3}{2}} \int_0^{+\infty} \frac{\varepsilon^{\frac{1}{2}} d\varepsilon}{e^{\frac{\varepsilon}{kT_c}} - 1} = \frac{2\pi}{h^3} (2mkT_c)^{\frac{3}{2}} \int_0^{+\infty} \frac{x_c^{\frac{1}{2}} dx_c}{e^{x_c} - 1}, \quad x_c = \frac{\varepsilon}{kT_c} \tag{8.34}$$

$$T_c = \frac{2\pi}{2.612^{\frac{3}{2}}} \frac{\hbar^2}{mk} n^{\frac{2}{3}} \tag{8.35}$$

3. 临界温度以下：$n_0(T)$ 不能忽略

$$n_{\varepsilon > 0}(T) = \frac{2\pi}{h^3} (2m)^{\frac{3}{2}} \int_0^{+\infty} \frac{\varepsilon^{\frac{1}{2}} d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1} = \frac{2\pi}{h^3} (2mkT)^{\frac{3}{2}} \int_0^{+\infty} \frac{x^{\frac{1}{2}} dx}{e^x - 1} = n \left(\frac{T}{T_c}\right)^2, \quad x = \frac{\varepsilon}{kT} \tag{8.36}$$

$$n = n_0(T) + n_{\varepsilon > 0}(T) = n_0(T) + n \left(\frac{T}{T_c}\right)^2 \tag{8.37}$$

4. ε_0 能级上的粒子数密度:

$$n_0(T) = n \left[1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}}\right], \quad T < T_c \tag{8.38}$$

5. 内能:

$$U = \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \int_0^{+\infty} \frac{\varepsilon^{\frac{3}{2}} d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1} = \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} (kT)^{\frac{5}{2}} \int_0^{+\infty} \frac{x^{\frac{3}{2}} dx}{e^x - 1} = 0.770 NkT \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \tag{8.39}$$

6. 热容:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{5}{2} \frac{U}{T} = 1.925 Nk \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \tag{8.40}$$

8.5 强简并理想 Fermi 气体

1. 化学势:

$$a_l = \frac{\omega_l}{e^{\frac{\varepsilon_l - \mu}{kT}} + 1}, \quad f(\varepsilon_l) = \frac{a_l}{\omega_l} = \frac{1}{e^{\frac{\varepsilon_l - \mu}{kT}} + 1} \tag{8.41}$$

$$n = \frac{N}{V} = \frac{1}{V} \sum_l \frac{\omega_l}{e^{\frac{\varepsilon_l - \mu}{kT}} + 1} \to \frac{4\pi}{h^3} (2m)^{\frac{3}{2}} \int_0^{+\infty} \frac{\varepsilon^{\frac{1}{2}} d\varepsilon}{e^{\frac{\varepsilon - \mu}{kT}} + 1} \tag{8.42}$$

2. $T = 0\text{K}$ 时的 Fermi 分布:

$$f(\varepsilon) = \begin{cases} 1 & \varepsilon < \mu_0 \\ 0 & \varepsilon > \mu_0 \end{cases} \tag{8.43}$$

$$n = \frac{4\pi}{h^3} (2m)^{\frac{3}{2}} \int_0^{\mu_0} \varepsilon^{\frac{1}{2}} d\varepsilon \Rightarrow \mu_0 = \frac{\hbar^2}{2m} \left(3\pi^2 n\right)^{\frac{2}{3}} \tag{8.44}$$

$$\varepsilon_F = \mu_0 = \frac{\hbar^2}{2m} \left(3\pi^2 n\right)^{\frac{2}{3}} \tag{8.45}$$

$$p_F = \sqrt{2m\varepsilon_F} = \hbar (3\pi^3 n)^{\frac{1}{3}} \tag{8.46}$$

$$T_F = \frac{\varepsilon_F}{k} = \frac{\hbar^2}{2mk} \left(3\pi^2 n\right)^{\frac{2}{3}} \tag{8.47}$$

(1) 内能:

$$U_0 = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}} \int_0^{\mu_0} \varepsilon^{\frac{3}{2}} \mathrm{d}\varepsilon = \frac{3}{5} N \mu_0 \tag{8.48}$$

(2) 压强:

$$p_0 = \frac{2}{3}\frac{U_0}{V} = \frac{2}{5} n \mu_0 \tag{8.49}$$

(3) 熵:

$$S_0 = 0 \tag{8.50}$$

3. $T > 0\mathrm{K}$ 时的 Fermi 分布:

$$f(\varepsilon) \sim \begin{cases} > \frac{1}{2} & \varepsilon < \mu \\ = \frac{1}{2} & \varepsilon = \mu \\ < \frac{1}{2} & \varepsilon > \mu \end{cases} \tag{8.51}$$

(1) 粒子数:

$$N = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}} \int_0^{+\infty} \frac{\varepsilon^{\frac{1}{2}} \mathrm{d}\varepsilon}{\mathrm{e}^{\frac{\varepsilon-\mu}{kT}} + 1} \approx \frac{2}{3}\frac{4\pi V}{h^3}(2m)^{\frac{3}{2}} \mu^{\frac{3}{2}} \left[1 + \frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2\right] \tag{8.52}$$

(2) 化学势:

$$\mu \approx \mu_0 \left[1 + \frac{\pi^2}{8}\left(\frac{kT}{\mu_0}\right)^2\right]^{-\frac{2}{3}} \approx \mu_0 \left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\mu_0}\right)^2\right] \tag{8.53}$$

(3) 内能:

$$U = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}} \int_0^{+\infty} \frac{\varepsilon^{\frac{3}{2}} \mathrm{d}\varepsilon}{\mathrm{e}^{\frac{\varepsilon-\mu}{kT}} + 1} \approx \frac{3}{5} N \mu_0 \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\mu_0}\right)^2\right] \tag{8.54}$$

(4) 热容:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = Nk\frac{\pi^2}{2}\frac{kT}{\mu_0} = \gamma_0 T \tag{8.55}$$

(5) 压强:

$$p = \frac{2}{3}\frac{U}{V} = \frac{2}{5} n \mu_0 \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\mu_0}\right)^2\right] \tag{8.56}$$

(6) 自由能:

$$F = G - pV = N\mu - \frac{2}{3}U \approx \frac{3}{5} N \mu_0 \left[1 - \frac{5\pi^2}{12}\left(\frac{kT}{\mu_0}\right)^2\right] \tag{8.57}$$

(7) 熵:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{\pi^2}{2} Nk \left(\frac{kT}{\mu_0}\right) \tag{8.58}$$

4. 自由电子气体条件:

$$\langle \varepsilon_{ee} \rangle \sim \frac{e^2}{\langle \delta r \rangle} \sim e^2 n^{\frac{1}{3}} \tag{8.59}$$

$$\langle \varepsilon_k \rangle \sim \frac{3}{5}\varepsilon_F \sim \frac{\hbar^2}{2m}(3\pi^2 n)^{\frac{2}{3}} \tag{8.60}$$

$$\langle \varepsilon_k \rangle \gg \langle \varepsilon_{ee} \rangle \Rightarrow n \gg \frac{1}{9\pi^4}\left(\frac{2me^2}{\hbar^2}\right)^3 \tag{8.61}$$

9 系综理论

9.1 系综理论

1. 系综微观态的数密度：

$$\int \widetilde{\rho}(q,p,t)\mathrm{d}\omega = \mathcal{N} \tag{9.1}$$

2. 系综微观态的概率密度：

$$\int \rho(q,p,t)\mathrm{d}\omega = 1, \quad \rho(q,p,t) = \frac{\widetilde{\rho}(q,p,t)}{\mathcal{N}} \tag{9.2}$$

3. 宏观量的系综平均：

$$\langle O\rangle = \int O(q,p,t)\rho(q,p,t)\mathrm{d}\omega \tag{9.3}$$

4. Liouville 定理：保守系

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \sum_i \frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i = \frac{\partial\rho}{\partial t} + \{\rho,\mathcal{H}\} = 0 \tag{9.4}$$

9.2 微正则系综

1. 微正则系综：孤立系处于平衡态
2. 概率密度：

$$\rho(q,p) = \begin{cases} \dfrac{1}{\varOmega(E,V,N)} & E \leqslant \mathcal{H}(q,p) \leqslant E+\Delta E \\ 0 & others. \end{cases} \tag{9.5}$$

3. 微观态数：

$$\varOmega(E,V,N) = \frac{1}{N!h^{Nr}}\int_{E\leqslant\mathcal{H}\leqslant E+\Delta E}\mathrm{d}\omega \tag{9.6}$$

4. 单原子理想气体的热力学函数：

(1) 微观态数：

$$\varOmega(E,V,N) = \frac{V^N}{N!h^{3N}}\int_{E\leqslant\mathcal{H}\leqslant E+\Delta E}\mathrm{d}p_1\cdots\mathrm{d}p_{3N} \tag{9.7}$$

$$\begin{aligned}\varSigma(E,V,N) &= \frac{V^N}{N!h^{3N}}\int_{\mathcal{H}\leqslant E}\mathrm{d}p_1\cdots\mathrm{d}p_{3N} = \frac{V^N}{N!h^{3N}}(2mE)^{\frac{3N}{2}}\int_{\sum_i x_i^2\leqslant 1}\mathrm{d}x_1\cdots\mathrm{d}x_{3N} \\ &= \frac{V^N}{N!h^{3N}}(2mE)^{\frac{3N}{2}}\frac{\pi^{\frac{3}{2}}}{\left(\frac{3N}{2}\right)!} = \frac{V^N}{N!h^{3N}\left(\frac{3N}{2}\right)!}(2\pi mE)^{\frac{3N}{2}}\end{aligned} \tag{9.8}$$

$$\varOmega(E,V,N) = \varSigma(E+\Delta E,V,N) - \varSigma(E,V,N) \approx \frac{\partial\varSigma}{\partial E}\Delta E = \frac{3N}{2}\frac{\Delta E}{E}\varSigma(E,V,N) \tag{9.9}$$

(2) 熵：

$$\begin{aligned}S(E,V,N) &= k\ln\varOmega(E,V,N) = Nk\ln\left[\frac{V}{N}\left(\frac{4\pi mE}{3h^2N}\right)^{\frac{3}{2}}\right] + \frac{5}{2}Nk + k\left[\ln\frac{3N}{2} + \ln\frac{\Delta E}{E}\right] \\ &\approx Nk\ln\left[\frac{V}{N}\left(\frac{4\pi mE}{3h^2N}\right)^{\frac{3}{2}}\right] + \frac{5}{2}Nk = Nk\left(\ln\frac{V}{N} - 3\ln\lambda_T + \frac{5}{2}\right)\end{aligned} \tag{9.10}$$

(3) 其他热力学函数：

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \Rightarrow E = \frac{3}{2}NkT \tag{9.11}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T} \Rightarrow pV = NkT \tag{9.12}$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} \Rightarrow \mu = kT\left(\ln\frac{N}{V} + 3\ln\lambda_T\right) \tag{9.13}$$

9.3 正则系综

1. 正则系综：系统与大热源接触达到平衡
2. 概率密度：

$$\rho_s(E_s) = \frac{\Omega_r(E_{tot} - E_s)}{\Omega(E_{tot})} \tag{9.14}$$

$$\ln \Omega_r(E_{tot} - E_s) \approx \ln \Omega_r(E_{tot}) - \frac{\partial \ln \Omega_r(E_{tot})}{\partial E_{tot}} E_s = \ln \Omega_r(E_{tot}) - \beta E_s \tag{9.15}$$

$$\rho_s(E_s) = \frac{1}{\Omega(E_{tot})} \mathrm{e}^{\ln \Omega_r(E_{tot} - E_s)} \approx \frac{\Omega_r(E_{tot})}{\Omega(E_{tot})} \mathrm{e}^{-\beta E_s} = \frac{1}{Z} \mathrm{e}^{-\beta E_s} \tag{9.16}$$

3. 配分函数：

$$Z(\beta, y_i) = \sum_s \mathrm{e}^{-\beta E_s} \tag{9.17}$$

4. 能级简并的的正则分布：

$$\rho_l = \frac{1}{Z} \omega_l \mathrm{e}^{-\beta E_l}, \quad Z = \sum_l \omega_l \mathrm{e}^{-\beta E_l} \tag{9.18}$$

$$\rho(q,p)\mathrm{d}\omega = \frac{1}{N! h^{Nr}} \frac{\mathrm{e}^{-\beta \mathcal{H}(q,p)}}{Z} \mathrm{d}\omega, \quad Z = \frac{1}{N! h^{Nr}} \int \mathrm{e}^{-\beta \mathcal{H}(q,p)} \mathrm{d}\omega \tag{9.19}$$

5. 内能：

$$U = \sum_s E_s \rho_s = \frac{1}{Z} \sum_s E_s \mathrm{e}^{-\beta E_s} = \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \sum_s \mathrm{e}^{-\beta E_s} \right) = -\frac{\partial}{\partial \beta} \ln Z \tag{9.20}$$

6. 广义力：

$$Y_i = \sum_s \frac{\partial E_s}{\partial y_i} \rho_s = \frac{1}{Z} \sum_s \frac{\partial E_s}{\partial y_i} \mathrm{e}^{-\beta E_s} = \frac{1}{Z} \left(-\frac{1}{\beta} \frac{\partial}{\partial y_i} \sum_s \mathrm{e}^{-\beta E_s} \right) = -\frac{1}{\beta} \frac{\partial}{\partial y} \ln Z \tag{9.21}$$

7. 参数 β：

$$\frac{1}{T}(\mathrm{d}U - \text{đ}W) = \mathrm{d}S, \quad \beta(\mathrm{d}U - \text{đ}W) = \left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \right) \Rightarrow \beta = \frac{1}{kT} \tag{9.22}$$

8. 熵：

$$S = k \left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \right) = k \left(\ln Z + \beta U \right) \tag{9.23}$$

9. 自由能：

$$F = -\frac{\partial}{\partial \beta} \ln Z - kT \left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \right) = -kT \ln Z \tag{9.24}$$

10. 能量涨落：

$$(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial}{\partial \beta} \frac{\sum_s E_s \mathrm{e}^{-\beta E_s}}{\sum_s \mathrm{e}^{-\beta E_s}} = -\frac{\partial U}{\partial \beta} = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V \tag{9.25}$$

9.4 单原子理想气体

1. 配分函数：

$$Z = \frac{1}{N! h^{3N}} \int \mathrm{e}^{-\beta \sum_i \varepsilon_i} \mathrm{d}\omega = \frac{1}{N!} \prod_{i=1}^N \left(\frac{1}{h^3} \int \mathrm{e}^{-\beta \varepsilon_i} \mathrm{d}\omega_i \right) = \frac{V^N}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}} = \frac{V^N}{N! \lambda_T^{3N}} \tag{9.26}$$

2. 压强：

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z = \frac{N}{\beta} \frac{\partial}{\partial V} \ln Z_1 = \frac{N}{V} kT \tag{9.27}$$

3. 内能：

$$U = -\frac{\partial}{\partial \beta} \ln Z = -N \frac{\partial}{\partial \beta} \ln Z_1 = \frac{3}{2} NkT \tag{9.28}$$

4. 熵：

$$S = k \left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \right) = Nk \left(\ln \frac{V}{N} - 3 \ln \lambda_T + \frac{5}{2} \right) \tag{9.29}$$

9.5 实际气体的物态方程

1. 单原子实际气体的 Hamilton 量：

$$\mathcal{H}=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\sum_{i<j}\phi_{ij} \tag{9.30}$$

2. 刚球势：

$$\phi(r)=\begin{cases}+\infty & r<r_0\\ -\phi_0\left(\frac{r_0}{r}\right)^6 & r\geqslant r_0\end{cases} \tag{9.31}$$

3. 配分函数：

$$Z=\frac{1}{N!h^{3N}}\int \mathrm{e}^{-\beta\mathcal{H}}\mathrm{d}\omega=\frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3N}{2}}Q(\beta,V)=\frac{1}{N!\lambda_T^{3N}}Q(\beta,V) \tag{9.32}$$

4. 位形积分：

$$\begin{aligned}Q(\beta,V)&=\int\prod_{i<j}\mathrm{e}^{-\beta\phi_{ij}}\mathrm{d}^3r_1\cdots\mathrm{d}^3r_N=\int\prod_{i<j}(1+f_{ij})\mathrm{d}^3r_1\cdots\mathrm{d}^3r_N\\&\approx\int\left(1+\sum_{i<j}f_{ij}\right)\mathrm{d}^3r_1\cdots\mathrm{d}^3r_N=V^N+\frac{N(N-1)}{2}\int f_{12}\mathrm{d}^3r_1\cdots\mathrm{d}^3r_N\\&=V^N+\frac{N(N-1)}{2}V^{N-2}\int f(r)\mathrm{d}^3r\mathrm{d}^3R\approx V^N\left(1+\frac{N^2}{2V}\int f(r)\mathrm{d}^3r\right)\end{aligned} \tag{9.33}$$

$$\ln Q=N\ln V+\ln\left(1+\frac{N^2}{2V}\int f(r)\mathrm{d}^3r\right)\approx N\ln V+\frac{N^2}{2V}\int f(r)\mathrm{d}^3r \tag{9.34}$$

5. 压强：

$$p=\frac{1}{\beta}\frac{\partial}{\partial V}\ln Q=\frac{NkT}{V}\left(1-\frac{N}{2V}\int f(r)\mathrm{d}^3r\right) \tag{9.35}$$

6. 第二位力系数：

$$\begin{aligned}B_2&=-\frac{N}{2}\int f(r)r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi=2\pi N\left(\int_0^{r_0}r^2\mathrm{d}r-\int_{r_0}^{+\infty}(\mathrm{e}^{-\phi(r)/kT}-1)r^2\mathrm{d}r\right)\\&\approx 2\pi N\left(\frac{r_0^3}{3}-\int_{r_0}^{+\infty}\phi_0\left(\frac{r_0}{r}\right)^6r^2\mathrm{d}r\right)=2\pi N\left(\frac{r_0^3}{3}-\phi_0\frac{r_0^3}{3kT}\right)=Nb-\frac{Na}{kT}\end{aligned} \tag{9.36}$$

$$b=\frac{2\pi}{3}r_0^3=4\cdot\frac{4\pi}{3}\left(\frac{r_0}{2}\right)^3,\quad a=\frac{2\pi}{3}r_0^3\phi_0 \tag{9.37}$$

7. 物态方程：

$$p=\frac{NkT}{V}\left(1+\frac{Nb}{V}\right)-\frac{N^2a}{V^2}\approx\frac{NkT}{V\left(1-\frac{Nb}{V}\right)}-\frac{N^2a}{V^2} \tag{9.38}$$

$$\left(p+\frac{N^2a}{V^2}\right)(V-Nb)=NkT \tag{9.39}$$

9.6 固体热容

1. 微振动势能展开：

$$\phi\approx\phi_0+\sum_i\left(\frac{\partial\phi}{\partial\xi_i}\right)_0\xi_i+\frac{1}{2}\sum_{ij}\left(\frac{\partial^2\phi}{\partial\xi_i\partial\xi_j}\right)_0\xi_i\xi_j=\phi_0+\frac{1}{2}\sum_{ij}\left(\frac{\partial^2\phi}{\partial\xi_i\partial\xi_j}\right)_0\xi_i\xi_j \tag{9.40}$$

2. Hamilton 量正则变换：

$$\mathcal{H}=\sum_{i=1}^{3N}\frac{p_{\xi_i}^2}{2m}+\frac{1}{2}\sum_{ij}\left(\frac{\partial^2\phi}{\partial\xi_i\partial\xi_j}\right)_0\xi_i\xi_j+\phi_0\to\frac{1}{2}\sum_{i=1}^{3N}(p_i^2+\omega_i^2q_i^2)+\phi_0 \tag{9.41}$$

3. 能量:

$$E_n=\sum_{i=1}^{3N}\left(n_i+\frac{1}{2}\right)\hbar\omega_i+\phi_0 \tag{9.42}$$

4. 配分函数:

$$Z=\mathrm{e}^{-\beta\phi_0}\sum_n \mathrm{e}^{-\beta\sum_i\left(n_i+\frac{1}{2}\right)\hbar\omega_i}=\mathrm{e}^{-\beta\phi_0}\prod_i\sum_n \mathrm{e}^{-\beta\left(n_i+\frac{1}{2}\right)\hbar\omega_i}=\mathrm{e}^{-\beta\phi_0}\prod_i\frac{\mathrm{e}^{-\frac{1}{2}x_i}}{1-\mathrm{e}^{-x_i}},\quad x_i=\beta\hbar\omega_i \tag{9.43}$$

5. 内能:

$$U=-\frac{\partial\ln Z}{\partial\beta}=U_0+\sum_{i=1}^{3N}\frac{\hbar\omega_i}{\mathrm{e}^{x_i}-1},\quad U_0=\phi_0+\sum_{i=1}^{3N}\frac{\hbar\omega_i}{2}<0 \tag{9.44}$$

6. 热容:

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=k\sum_{i=1}^{3N}x_i^2\frac{\mathrm{e}^{x_i}}{\left(\mathrm{e}^{x_i}-1\right)^2}\xrightarrow{x_i\to 0}k\sum_{i=1}^{3N}1=3Nk \tag{9.45}$$

7. Einstein 近似:

$$\omega_i=\omega_E,\quad k\theta_E=\hbar\omega_E,\quad x_E=\frac{\theta_E}{T} \tag{9.46}$$

$$C_V=3Nkx_E^2\frac{\mathrm{e}^{x_E}}{\left(\mathrm{e}^{x_E}-1\right)^2}\approx\begin{cases}3Nk & x_E\to 0\\ 3Nkx_E^2\mathrm{e}^{-x_E}\to 0 & x_E\to+\infty\end{cases} \tag{9.47}$$

8. Debye 近似:

$$D(\omega)\mathrm{d}\omega=\frac{V}{(2\pi)^3}4\pi k^2\mathrm{d}k=\frac{V}{2\pi^2}\left(\frac{\omega}{c_l}\right)^2\frac{\mathrm{d}\omega}{c_l}+2\frac{V}{2\pi^2}\left(\frac{\omega}{c_t}\right)^2\frac{\mathrm{d}\omega}{c_t}=B\omega^2\mathrm{d}\omega,\quad B=\frac{V}{2\pi^2}\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right) \tag{9.48}$$

$$\int_0^{\omega_D}B\omega^2\mathrm{d}\omega=3N\Rightarrow\omega_D^3=\left(\frac{9N}{B}\right),\quad k\theta_D=\hbar\omega_D,\quad x_D=\frac{\theta_D}{T},\quad \mathcal{D}(x_D)=\frac{3}{x_D^2}\int_0^{x_D}\frac{x^3\mathrm{d}x}{\mathrm{e}^x-1} \tag{9.49}$$

$$U=U_0+B\int_0^{\omega_D}\frac{\hbar\omega^3}{\mathrm{e}^x-1}\mathrm{d}\omega=U_0+3NkT\mathcal{D}(x_D)\approx\begin{cases}U_0+3NkT & x_D\to 0\\ U_0+3Nk\dfrac{\pi^4}{5}\dfrac{T^4}{\theta_D^3} & x_D\to+\infty\end{cases} \tag{9.50}$$

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V\approx\begin{cases}3Nk & x_D\to 0\\ 3Nk\dfrac{4\pi^4}{5}\left(\dfrac{T}{\theta_D}\right)^3 & x_D\to+\infty\end{cases} \tag{9.51}$$

9.7 巨正则系综

1. 巨正则系综:系统与大热源和粒子源接触达到平衡
2. 概率密度:

$$\rho_s(N_s,E_s)=\frac{\mathit{\Omega}_r(N_{tot}-N_s,E_{tot}-E_s)}{\mathit{\Omega}(E_{tot},N_{tot})} \tag{9.52}$$

$$\begin{aligned}\ln\mathit{\Omega}_r(N_{tot}-N_s,E_{tot}-E_s)&\approx\ln\mathit{\Omega}_r(N_{tot},E_{tot})-\frac{\partial\ln\mathit{\Omega}_r(N_{tot},E_{tot})}{\partial N_{tot}}N_s-\frac{\partial\ln\mathit{\Omega}_r(N_{tot},E_{tot})}{\partial E_{tot}}E_s\\&=\ln\mathit{\Omega}_r(N_{tot},E_{tot})-\alpha N_s-\beta E_s\end{aligned} \tag{9.53}$$

$$\rho_s(N_s,E_s)=\frac{1}{\mathit{\Omega}(N_{tot},E_{tot})}\mathrm{e}^{\ln\mathit{\Omega}_r(N_{tot}-N_s,E_{tot}-E_s)}\approx\frac{\mathit{\Omega}_r(N_{tot},E_{tot})}{\mathit{\Omega}(N_{tot},E_{tot})}\mathrm{e}^{-\alpha N_s-\beta E_s}=\frac{1}{\mathit{\Xi}}\mathrm{e}^{-\alpha N_s-\beta E_s} \tag{9.54}$$

3. 巨配分函数:

$$\mathit{\Xi}(\alpha,\beta,y_i)=\sum_{N=0}^{+\infty}\sum_s\mathrm{e}^{-\alpha N-\beta E_s}=\sum_{N=0}^{+\infty}\mathrm{e}^{-\alpha N}Z(\beta,y_i) \tag{9.55}$$

4. 能级简并的巨正则分布:

$$\rho_{Nl}=\frac{1}{\Xi}\omega_l\mathrm{e}^{-\alpha N-\beta E_l},\quad \Xi=\sum_{N=0}^{+\infty}\sum_l\omega_l\mathrm{e}^{-\alpha N-\beta E_l}\tag{9.56}$$

$$\rho_N(q,p)\mathrm{d}\omega=\frac{1}{N!h^{Nr}}\frac{\mathrm{e}^{-\alpha N-\beta\mathcal{H}(q,p)}}{\Xi}\mathrm{d}\omega,\quad \Xi=\sum_{N=0}^{+\infty}\frac{\mathrm{e}^{-\alpha N}}{N!h^{Nr}}\int\mathrm{e}^{-\beta\mathcal{H}(q,p)}\mathrm{d}\omega\tag{9.57}$$

5. 粒子数:

$$\langle N\rangle=\sum_N\sum_s N\rho_{Ns}=\frac{1}{\Xi}\sum_N\sum_s N\mathrm{e}^{-\alpha N-\beta E_s}=\frac{1}{\Xi}\left(-\frac{\partial}{\partial\alpha}\sum_N\sum_s\mathrm{e}^{-\alpha N-\beta E_s}\right)=-\frac{\partial}{\partial\alpha}\ln\Xi\tag{9.58}$$

6. 内能:

$$U=\sum_N\sum_s E_s\rho_s=\frac{1}{\Xi}\sum_N\sum_s E_s\mathrm{e}^{-\alpha N-\beta E_s}=\frac{1}{\Xi}\left(-\frac{\partial}{\partial\beta}\sum_N\sum_s\mathrm{e}^{-\alpha N-\beta E_s}\right)=-\frac{\partial}{\partial\beta}\ln\Xi\tag{9.59}$$

7. 广义力:

$$Y_i=\sum_N\sum_s\left(\frac{\partial E_s}{\partial y_i}\right)\rho_s=\frac{1}{\Xi}\sum_N\sum_s\frac{\partial E_s}{\partial y_i}\mathrm{e}^{-\alpha N-\beta E_s}=\frac{1}{\Xi}\left(-\frac{1}{\beta}\sum_N\sum_s\mathrm{e}^{-\alpha N-\beta E_s}\right)=-\frac{1}{\beta}\frac{\partial}{\partial y_i}\ln\Xi\tag{9.60}$$

8. 参数 α, β:

$$\frac{1}{T}(\mathrm{d}U-\text{đ}W-\mu\mathrm{d}\langle N\rangle)=\mathrm{d}S,\quad \beta\left(\mathrm{d}U-\text{đ}W+\frac{\alpha}{\beta}\mathrm{d}\langle N\rangle\right)=\mathrm{d}\left(\ln\Xi-\alpha\frac{\partial}{\partial\alpha}\ln\Xi-\beta\frac{\partial}{\partial\beta}\ln\Xi\right)\tag{9.61}$$

$$\Rightarrow\beta=\frac{1}{kT},\quad \alpha=-\frac{\mu}{kT}\tag{9.62}$$

9. 熵:

$$S=k\left(\ln\Xi-\alpha\frac{\partial}{\partial\alpha}\ln\Xi-\beta\frac{\partial}{\partial\beta}\ln\Xi\right)=k(\ln\Xi+\alpha\langle N\rangle+\beta U)\tag{9.63}$$

10. 巨热力势:

$$J=U-kT(\ln\Xi+\alpha\langle N\rangle+\beta U)-\alpha kT\langle N\rangle=-kT\ln\Xi\tag{9.64}$$

11. 粒子数涨落:

$$\begin{aligned}(\Delta N)^2=\langle N^2\rangle-\langle N\rangle^2&=-\frac{\partial}{\partial\alpha}\frac{\sum_N\sum_s N\mathrm{e}^{-\alpha N-\beta E_s}}{\sum_N\sum_s\mathrm{e}^{-\alpha N-\beta E_s}}\\&=-\left(\frac{\partial\langle N\rangle}{\partial\alpha}\right)_{T,V}=kT\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V}=\frac{kT}{V}\langle N\rangle^2\kappa_T\end{aligned}\tag{9.65}$$

9.8 单原子理想气体

1. 巨配分函数:

$$\Xi=\sum_{N=0}^{+\infty}\mathrm{e}^{-\alpha N}Z=\sum_{N=0}^{+\infty}\frac{\mathrm{e}^{-\alpha N}}{N!h^{3N}}\int\mathrm{e}^{-\beta\sum_i\varepsilon_i}\mathrm{d}\omega=\sum_{N=0}^{+\infty}\frac{\mathrm{e}^{-\alpha N}V^N}{N!\lambda_T^{3N}}=\exp\left(\frac{\mathrm{e}^{-\alpha}V}{\lambda_T^3}\right)\tag{9.66}$$

2. 粒子数:

$$\langle N\rangle=-\frac{\partial}{\partial\alpha}\ln\Xi=\ln\Xi=\frac{\mathrm{e}^{-\alpha}V}{\lambda_T^3}\tag{9.67}$$

3. 压强:

$$p=\frac{1}{\beta}\frac{\partial}{\partial V}\ln\Xi=\frac{1}{\beta V}\ln\Xi=\frac{N}{V}kT\tag{9.68}$$

4. 内能:

$$U=-\frac{\partial}{\partial\beta}\ln\Xi=\frac{3}{2\beta}\ln\Xi=\frac{3}{2}NkT\tag{9.69}$$

5. 熵:

$$S=k(\ln\Xi+\alpha\langle N\rangle+\beta U)=Nk\left(\ln\frac{V}{N}-3\ln\lambda_T+\frac{5}{2}\right)\tag{9.70}$$

9.9 固体表面吸附率

1. 巨配分函数:

$$\Xi=\sum_{N=0}^{N_0}\sum_s \mathrm{e}^{-\alpha N-\beta E_{Ns}}=\sum_{N=0}^{N_0}\frac{N_0!}{N!(N-N_0)!}\mathrm{e}^{\beta(\mu+\varepsilon_0)N}=\left(1+\mathrm{e}^{\beta(\mu+\varepsilon_0)}\right)^{N_0} \tag{9.71}$$

2. 被吸附的粒子数:

$$\langle N\rangle=-\frac{\partial}{\partial\alpha}\ln\Xi=\frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\Xi=N_0\frac{\mathrm{e}^{\beta(\mu+\varepsilon_0)}}{1+\mathrm{e}^{\beta(\mu+\varepsilon_0)}}=\frac{N_0}{1+\mathrm{e}^{-\beta(\mu+\varepsilon_0)}} \tag{9.72}$$

3. 化学势:

$$\mu=-kT\alpha=kT\ln\left(\frac{\langle N\rangle}{V}\lambda_T^3\right)=kT\ln\left(n\lambda_T^3\right) \tag{9.73}$$

4. 吸附率:

$$\theta=\frac{\langle N\rangle}{N_0}=\frac{1}{1+\mathrm{e}^{-\beta(\mu+\varepsilon_0)}}=\frac{1}{1+\frac{kT}{p}\lambda_T^3\mathrm{e}^{-\frac{\varepsilon_0}{kT}}} \tag{9.74}$$

9.10 近独立粒子的平均分布

1. Maxwell-Boltzmann 分布:

$$\begin{aligned}\Xi&=\sum_{N=0}^{+\infty}\sum_s \mathrm{e}^{-\alpha N-\beta E_s}=\sum_{N=0}^{+\infty}\frac{1}{N!}\sum_{\{\varepsilon_i\}}\mathrm{e}^{-\sum_{i=1}^N(\alpha+\beta\varepsilon_i)}=\sum_{N=0}^{+\infty}\frac{1}{N!}\prod_{i=1}^{N}\sum_{\varepsilon_i}\mathrm{e}^{-\alpha-\beta\varepsilon_i}\\&=\sum_{N=0}^{+\infty}\frac{1}{N!}\left(\sum_{\varepsilon_i}\mathrm{e}^{-\alpha-\beta\varepsilon_i}\right)^N=\exp\left(\sum_{\varepsilon_i}\mathrm{e}^{-\alpha-\beta\varepsilon_i}\right)\end{aligned} \tag{9.75}$$

$$\langle N\rangle=-\frac{\partial}{\partial\alpha}\ln\Xi=\sum_{\varepsilon_i}\mathrm{e}^{-\alpha-\beta\varepsilon_i}=\sum_l\omega_l\mathrm{e}^{-\alpha-\beta\varepsilon_l}=\sum_l\langle a_l\rangle \tag{9.76}$$

$$\langle a_l\rangle=\omega_l\mathrm{e}^{-\alpha-\beta\varepsilon_l} \tag{9.77}$$

2. Bose-Einstein 分布:

$$\begin{aligned}\Xi&=\sum_{N=0}^{+\infty}\sum_s \mathrm{e}^{-\alpha N-\beta E_s}=\sum_{N=0}^{+\infty}\sum_{E_s}\mathrm{e}^{-\sum_s(\alpha+\beta\varepsilon_s)a_s}=\sum_{\{a_s\}}\prod_s\mathrm{e}^{-(\alpha+\beta\varepsilon_s)a_s}=\prod_s\sum_{a_s=0}^{+\infty}\mathrm{e}^{-(\alpha+\beta\varepsilon_s)a_s}\\&=\prod_s\left(1-\mathrm{e}^{-(\alpha+\beta\varepsilon_s)a_s}\right)^{-1}=\prod_l\left(1-\mathrm{e}^{-\alpha-\beta\varepsilon_l}\right)^{-\omega_l}\end{aligned} \tag{9.78}$$

$$\langle N\rangle=-\frac{\partial}{\partial\alpha}\ln\Xi=\sum_l\frac{\omega_l}{\mathrm{e}^{\alpha+\beta\varepsilon_l}-1}=\sum_l\langle a_l\rangle \tag{9.79}$$

$$\langle a_l\rangle=\frac{\omega_l}{\mathrm{e}^{\alpha+\beta\varepsilon_l}-1} \tag{9.80}$$

3. Fermi-Dirac 分布:

$$\begin{aligned}\Xi&=\sum_{N=0}^{+\infty}\sum_s \mathrm{e}^{-\alpha N-\beta E_s}=\sum_{N=0}^{+\infty}\sum_{E_s}\mathrm{e}^{-\sum_s(\alpha+\beta\varepsilon_s)a_s}=\sum_{\{a_s\}}\prod_s\mathrm{e}^{-(\alpha+\beta\varepsilon_s)a_s}=\prod_s\sum_{a_s=0}^{1}\mathrm{e}^{-(\alpha+\beta\varepsilon_s)a_s}\\&=\prod_s\left(1+\mathrm{e}^{-\alpha-\beta\varepsilon_s}\right)=\prod_l\left(1+\mathrm{e}^{-\alpha-\beta\varepsilon_l}\right)^{\omega_l}\end{aligned} \tag{9.81}$$

$$\langle N\rangle=-\frac{\partial}{\partial\alpha}\ln\Xi=\sum_l\frac{\omega}{\mathrm{e}^{\alpha+\beta\varepsilon_l}+1}=\sum_l\langle a_l\rangle \tag{9.82}$$

$$\langle a_l\rangle=\frac{\omega_l}{\mathrm{e}^{\alpha+\beta\varepsilon_l}+1} \tag{9.83}$$

10 相变和临界现象的统计理论

10.1 远离临界点的平均场近似

1. Ising 模型的 Hamilton 量：

$$\mathcal{H} = -J\sum_{ij}{}'\sigma_i\sigma_j - \mu B\sum_i \sigma_i \tag{10.1}$$

2. 平均场近似：

$$\mathcal{H} = -\sum_i \mu\sigma_i B_{\text{eff}} = -\sum_i \mu\sigma_i \left(B + \frac{J}{\mu}\sum_j{}'\sigma_j\right) \to -\sum_i \mu\sigma_i \left(B + \frac{J}{\mu}z\left\langle\sigma\right\rangle\right) \tag{10.2}$$

3. 配分函数：

$$Z = \sum_{\{\sigma_i\}} \mathrm{e}^{-\beta\mathcal{H}} = \prod_i \sum_{\sigma_i=\pm 1} \mathrm{e}^{\beta\mu\sigma_i B_{\text{eff}}} = \left[2\cosh\left(\frac{\mu B}{kT} + \frac{Jz}{kT}\left\langle\sigma\right\rangle\right)\right]^N \tag{10.3}$$

4. 总磁矩：

$$m = \frac{1}{\beta}\frac{\partial}{\partial B}\ln Z = N\mu\tanh\left(\frac{\mu B}{kT} + \frac{Jz}{kT}\left\langle\sigma\right\rangle\right) = N\mu\left\langle\sigma\right\rangle \tag{10.4}$$

5. 自旋方向的自洽方程：

$$\left\langle\sigma\right\rangle = \tanh\left(\frac{\mu B}{kT} + \frac{Jz}{kT}\left\langle\sigma\right\rangle\right) \tag{10.5}$$

6. 无外磁场时：

$$\left\langle\sigma\right\rangle = \begin{cases} 0 & T > T_c \\ \pm\left\langle\sigma_0\right\rangle & T < T_c \end{cases}, \quad T_c = \frac{Jz}{k} \tag{10.6}$$

10.2 临界点附近的重整化群

1. 一维 Ising 模型的 Hamilton 量：无外磁场

$$\mathcal{H} = -J\sum_i \sigma_i\sigma_{i+1} \tag{10.7}$$

2. 配分函数：

$$Z = \sum_{\{\sigma_i\}} \mathrm{e}^{-\beta\mathcal{H}} = \sum_{\{\sigma_i\}} \mathrm{e}^{K\sum_i \sigma_i\sigma_{i+1}} = \sum_{\sigma_1\sigma_3\cdots}\sum_{\sigma_2\sigma_4\cdots} \mathrm{e}^{K\sigma_2(\sigma_1+\sigma_3)}\mathrm{e}^{K\sigma_4(\sigma_3+\sigma_5)}\cdots, \quad K = \beta J \tag{10.8}$$

3. 重整化群变换：

$$\sum_{\sigma_2} \mathrm{e}^{K\sigma_2(\sigma_1+\sigma_3)} = \mathrm{e}^{K(\sigma_1+\sigma_3)} + \mathrm{e}^{-K(\sigma_1+\sigma_3)} = \mathrm{e}^{K'\sigma_1\sigma_3+g} \tag{10.9}$$

$$\mathrm{e}^{2K} + \mathrm{e}^{-2K} = \mathrm{e}^{K'+g}, \quad 2 = \mathrm{e}^{g-K'} \tag{10.10}$$

$$K' = \frac{1}{2}\ln\cosh 2K < K, \quad \mathrm{e}^{2g} = 4\cosh 2K \tag{10.11}$$

4. 重整化群变换后的配分函数：

$$Z(N,K) = \mathrm{e}^{\frac{N}{2}g(K)}\sum_{\sigma_1\sigma_3\cdots} \mathrm{e}^{K'(\sigma_1\sigma_3+\sigma_3\sigma_5+\cdots)} = \mathrm{e}^{\frac{N}{2}g(K)}Z\left(\frac{N}{2}, K'\right) \tag{10.12}$$

5. 重整化群变换的不动点：临界点对应于重整化群的不稳定不动点

$$K^* = R(K^*) \Rightarrow K^* = \frac{1}{2}\ln\cosh 2K^* \Rightarrow K^* = +\infty \Rightarrow T_c = 0 \tag{10.13}$$

10.3 Ising 模型的严格解

1. 一维 Ising 模型的 Hamilton 量：

$$\mathcal{H} = -J\sum_i \sigma_i\sigma_{i+1} - \mu B\sum_i \sigma_i = -J\sum_i \sigma_i\sigma_{i+1} - \frac{1}{2}\mu B\sum_i(\sigma_i+\sigma_{i+1}) \tag{10.14}$$

2. 配分函数：

$$Z = \sum_{\{\sigma_i\}}\prod_i \mathrm{e}^{\beta J\sigma_i\sigma_{i+1}+\frac{1}{2}\beta\mu B(\sigma_1+\sigma_{i+1})} = \sum_{\{\sigma_i\}}\prod_i \langle\sigma_i|\hat{P}|\sigma_{i+1}\rangle = \sum_{\sigma_1}\langle\sigma_1|\hat{P}^N|\sigma_1\rangle = \mathrm{tr}(\boldsymbol{P}^N) \tag{10.15}$$

$$\boldsymbol{P} = \begin{pmatrix} \mathrm{e}^{\beta(J+\mu B)} & \mathrm{e}^{-\beta J} \\ \mathrm{e}^{-\beta J} & \mathrm{e}^{\beta(J-\mu B)} \end{pmatrix} \tag{10.16}$$

$$\lambda_\pm = \mathrm{e}^{\beta J}\left(\cosh\beta\mu B \pm \sqrt{\sinh^2\beta\mu B + \mathrm{e}^{-4\beta J}}\right) \tag{10.17}$$

$$Z = \lambda_+^N + \lambda_-^N = \lambda_+^N\left[1+\left(\frac{\lambda_-}{\lambda_+}\right)^N\right] \xrightarrow{N\to+\infty} \lambda_+^N \tag{10.18}$$

3. 零场磁化强度：

$$\mathscr{M} = \frac{1}{N\beta}\frac{\partial}{\partial B}\ln Z\bigg|_{B=0} = \frac{1}{\beta}\frac{\partial}{\partial B}\ln\lambda_+\bigg|_{B=0} = \frac{\mu\sinh\beta\mu B}{\sqrt{\sinh^2\beta\mu B+\mathrm{e}^{-4\beta J}}}\bigg|_{B=0} = 0 \tag{10.19}$$

$\langle\sigma\rangle = 0$，序参量始终为 0，不可能出现顺磁-铁磁相变

4. 零场磁化率：

$$\chi_m^0 = \left(\frac{\partial\mathscr{M}}{\partial B}\right)_T\bigg|_{B=0} = \frac{\mu\left[\beta\mu\cosh\beta\mu B(\sinh^2\beta\mu B+\mathrm{e}^{-4\beta J}+\frac{1}{2}\sinh\beta\mu B)\right]}{(\sinh^2\beta\mu B+\mathrm{e}^{-4\beta J})^{\frac{3}{2}}}\bigg|_{B=0} = \beta\mu^2\mathrm{e}^{2\beta J} \tag{10.20}$$

10.4 涨落关联的作用

1. 平均场近似忽略了涨落关联的作用：

$$\sigma_i = \langle\sigma\rangle + \delta_i, \quad \langle\sigma\rangle = 0 \tag{10.21}$$

$$\sigma_i\sigma_{i+1} = \langle\sigma\rangle^2 + (\delta_i+\delta_{i+1})\langle\sigma\rangle + \delta_i\delta_{i+1} \approx (\sigma_i+\sigma_{i+1})\langle\sigma\rangle - \langle\sigma\rangle^2 \tag{10.22}$$

$$g(i,j) = \langle\delta_i\delta_j\rangle = \langle(\sigma_i-\langle\sigma\rangle)(\sigma_j-\langle\sigma\rangle)\rangle = \langle\sigma_i\sigma_j\rangle - \langle\sigma\rangle^2 \tag{10.23}$$

2. 一维 Ising 模型的 Hamilton 量：无外磁场

$$\mathcal{H} = -\sum_{i=1}^N J_i\sigma_i\sigma_{i+1} \tag{10.24}$$

3. 配分函数：

$$Z = \sum_{\{\sigma_i\}}\mathrm{e}^{\beta\sum_{i=1}^N J_i\sigma_i\sigma_{i+1}} = 2\cosh\beta J_{N-1}\sum_{\{\sigma_i\}}\mathrm{e}^{\beta\sum_{i=1}^{N-1}J_i\sigma_i\sigma_{i+1}} = 2^N\prod_{i=1}^{N-1}\cosh\beta J_i \tag{10.25}$$

4. 自旋关联函数：

$$\begin{aligned} g(i,j) = \langle\sigma_i\sigma_j\rangle &= \frac{1}{Z}\sum_{\{\sigma_i\}}(\sigma_i\sigma_{i+1}\sigma_{i+1}\cdots\sigma_{j-1}\sigma_{j-1}\sigma_j)\mathrm{e}^{\beta\sum_{i=1}^N J_i\sigma_i\sigma_{i+1}} \\ &= \frac{1}{Z}\sum_{\{\sigma_i\}}\frac{\partial}{\beta\partial J_i}\cdots\frac{\partial}{\beta\partial J_{j-1}}\mathrm{e}^{\beta\sum_{i=1}^N J_i\sigma_i\sigma_{i+1}} = \frac{1}{Z}\frac{\partial}{\beta\partial J_i}\cdots\frac{\partial}{\beta\partial J_{j-1}}Z \\ &= \prod_{k=i}^{j-1}\tanh\beta J_k = \tanh^{j-i}\beta J = \mathrm{e}^{-\frac{j-i}{\xi}}, \quad \xi = -\ln^{-1}\tanh\beta J \end{aligned} \tag{10.26}$$

5. 零场磁化率：

$$\chi_m^0 = \left(\frac{\partial\mathscr{M}}{\partial B}\right)_T = \beta\mu^2\sum_j(\langle\sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle) = \beta\mu^2\sum_j\mathrm{e}^{-\frac{j-i}{\xi}} \to \beta\mu^2\int_0^{+\infty}\mathrm{e}^{-\frac{x}{\xi}}\mathrm{d}x = \beta\mu^2\xi \tag{10.27}$$

11 涨落理论

11.1 涨落的准热力学理论

1. 微正则系综的涨落：

$$\langle S\rangle = k\ln\Omega_m,\quad S = k\ln\Omega \Rightarrow \Omega = \Omega_m\exp\left(\frac{\Delta S}{k}\right) \tag{11.1}$$

2. 正则系综的涨落：

$$\Delta E_s + \Delta E_r = 0,\quad \Delta V_s + \Delta V_r = 0,\quad \Delta S = \Delta S_s + \Delta S_r \tag{11.2}$$

$$\Omega = \Omega_m\exp\left(\frac{\Delta S}{k}\right) = \Omega_m\exp\left(\frac{T\Delta S_s + \Delta E_r + p\Delta V_r}{kT}\right) = \Omega_m\exp\left(-\frac{\Delta E_s - T\Delta S_s + p\Delta V_s}{kT}\right) \tag{11.3}$$

(1) 小涨落时：

$$\begin{aligned}\Delta E &= E(S+\Delta S, V+\Delta V) - E(S,V)\\ &\approx T\Delta S - p\Delta V + \frac{1}{2}\left[\left(\frac{\partial T}{\partial S}\Delta S + \frac{\partial T}{\partial V}\Delta V\right)\Delta S - \left(\frac{\partial p}{\partial S}\Delta S + \frac{\partial p}{\partial V}\Delta V\right)\Delta V\right]\\ &= T\Delta S - p\Delta V + \frac{1}{2}(\Delta T\Delta S - \Delta p\Delta V)\end{aligned} \tag{11.4}$$

$$\Omega = \Omega_m\exp\left(-\frac{\Delta T\Delta S - \Delta p\Delta V}{2kT}\right) \tag{11.5}$$

(2) $T-V$ 涨落：

$$\Delta S = \frac{C_V}{T}\Delta T + \left(\frac{\partial S}{\partial V}\right)_T\Delta V,\quad \Delta p = \left(\frac{\partial p}{\partial T}\right)_V\Delta T - \frac{1}{V\kappa_T}\Delta V \tag{11.6}$$

$$\Delta T\Delta S - \Delta p\Delta V = \frac{C_V}{T}(\Delta T)^2 + \frac{1}{V\kappa_T}(\Delta V)^2 \tag{11.7}$$

$$\Omega(\Delta T,\Delta V) = \Omega_m\exp\left(-\frac{C_V}{2kT^2}(\Delta T)^2 - \frac{1}{2kTV\kappa_T}(\Delta V)^2\right) \tag{11.8}$$

$$\langle(\Delta T)^2\rangle = \frac{\int_{-\infty}^{+\infty}(\Delta T)^2\exp\left(-\frac{C_V}{2kT^2}(\Delta T)^2\right)\mathrm{d}(\Delta T)}{\int_{-\infty}^{+\infty}\exp\left(-\frac{C_V}{2kT^2}(\Delta T)^2\right)\mathrm{d}(\Delta T)} = \frac{kT^2}{C_V} \Rightarrow \frac{\sqrt{\langle(\Delta T)^2\rangle}}{T} = \sqrt{\frac{k}{C_V}} \sim \frac{1}{\sqrt{N}} \tag{11.9}$$

$$\langle(\Delta V)^2\rangle = \frac{\int_{-\infty}^{+\infty}(\Delta V)^2\exp\left(-\frac{1}{2kTV\kappa_T}(\Delta V)^2\right)\mathrm{d}(\Delta V)}{\int_{-\infty}^{+\infty}\exp\left(-\frac{1}{2kTV\kappa_T}(\Delta V)^2\right)\mathrm{d}(\Delta V)} = kTV\kappa_T \Rightarrow \frac{\langle(\Delta V)^2\rangle}{V^2} = \frac{kT}{V}\kappa_T \tag{11.10}$$

$$\langle\Delta T\Delta V\rangle = 0 \tag{11.11}$$

(3) $T-p$ 涨落：

$$\Delta p = p\beta\Delta T - \frac{1}{V\kappa_T}\Delta V \tag{11.12}$$

$$\langle(\Delta p)^2\rangle = p^2\beta^2\langle(\Delta T)^2\rangle - 2\frac{p\beta}{N\kappa_T}\langle\Delta T\Delta V\rangle + \frac{1}{V^2\kappa_T^2}\langle(\Delta V)^2\rangle = p^2\beta^2\frac{kT^2}{C_V} + \frac{kT}{V\kappa_T} = \frac{kT}{V\kappa_s} \tag{11.13}$$

$$\langle\Delta T\Delta p\rangle = p\beta\langle(\Delta T)^2\rangle - \frac{1}{V\kappa_T}\langle\Delta T\Delta V\rangle = p\beta\frac{kT^2}{C_V} \tag{11.14}$$

$$\langle\Delta V\Delta p\rangle = p\beta\langle\Delta T\Delta V\rangle - \frac{1}{V\kappa_T}\langle(\Delta V)^2\rangle = -kT \tag{11.15}$$

(4) 大涨落时：临界点邻域，$\kappa_T\to+\infty$，令 T 不变

$$\begin{aligned}\Delta F &= F(T, V+\Delta V) - F(T,V)\\ &\approx -p\Delta V - \frac{1}{2!}\left(\frac{\partial p}{\partial V}\right)_T(\Delta V)^2 - \frac{1}{3!}\left(\frac{\partial^2 p}{\partial V^2}\right)_T(\Delta V)^3 - \frac{1}{4!}\left(\frac{\partial^3 p}{\partial V^3}\right)_T(\Delta V)^4\\ &= -p\Delta V - \frac{1}{24}\left(\frac{\partial^3 p}{\partial V^3}\right)_T(\Delta V)^4\end{aligned} \tag{11.16}$$

$$\Omega(\Delta V)=\Omega_m\exp\left(-\frac{\Delta F+p\Delta V}{kT}\right)=\Omega_m\exp\left(\frac{1}{24kT}\left(\frac{\partial^3 p}{\partial V^3}\right)_T(\Delta V)^4\right) \tag{11.17}$$

$$\begin{aligned}\langle(\Delta V)^2\rangle&=\frac{\int_0^{+\infty}x^2\mathrm{e}^{-\alpha x^4}\mathrm{d}x}{\int_0^{+\infty}\mathrm{e}^{-\alpha x^4}\mathrm{d}x}=\frac{\int_0^{+\infty}\alpha^{-\frac{1}{2}}\mathrm{e}^{-\xi}\xi^{\frac{3}{4}-1}\mathrm{d}\xi}{\int_0^{+\infty}\mathrm{e}^{-\xi}\xi^{\frac{1}{4}-1}\mathrm{d}\xi},\quad x=\Delta V,\quad \xi=\alpha x^4\\&=\frac{\Gamma\left(\frac{3}{4}\right)}{\Gamma\left(\frac{1}{4}\right)}\alpha^{-\frac{1}{2}}=0.3380\left[-\frac{1}{24kT}\left(\frac{\partial^3 p}{\partial V^3}\right)_T\right]^{-\frac{1}{2}}\end{aligned} \tag{11.18}$$

3. 巨正则系综的涨落:

$$\Delta E_s+\Delta E_r=0,\quad \Delta V_s+\Delta V_r=0,\quad \Delta N_s+\Delta N_r=0,\quad \Delta S=\Delta S_s+\Delta S_r \tag{11.19}$$

$$\Omega=\Omega_m\exp\left(\frac{T\Delta S_s+\Delta E_r+p\Delta V_r-\mu\Delta N_r}{kT}\right)=\Omega_m\exp\left(-\frac{\Delta E_s-T\Delta S_s+p\Delta V_s-\mu\Delta N_s}{kT}\right) \tag{11.20}$$

(1) 小涨落时:

$$\begin{aligned}\Delta E&=E(S+\Delta S,V+\Delta V,N+\Delta N)-E(S,V,N)\\&\approx T\Delta S-p\Delta V+\mu\Delta N+\frac{1}{2}(\Delta T\Delta S-\Delta p\Delta V+\Delta\mu\Delta N)\end{aligned} \tag{11.21}$$

$$\Omega=\Omega_m\exp\left(-\frac{\Delta S\Delta T-\Delta p\Delta V+\Delta\mu\Delta N}{2kT}\right) \tag{11.22}$$

(2) $T-N$ 涨落：令 V 不变

$$\Delta S=\frac{C_V}{T}\Delta T-\left(\frac{\partial\mu}{\partial T}\right)_{V,N}\Delta N,\quad \Delta\mu=\left(\frac{\partial\mu}{\partial T}\right)_{V,N}\Delta T+\left(\frac{\partial\mu}{\partial N}\right)_{V,T}\Delta N \tag{11.23}$$

$$\Delta S\Delta T-\Delta p\Delta V+\Delta\mu\Delta N=\frac{C_V}{T}(\Delta T)^2-\left(\frac{\partial\mu}{\partial N}\right)_{V,T}(\Delta N)^2 \tag{11.24}$$

$$\Omega(\Delta T,\Delta V)=\Omega_m\exp\left(-\frac{C_V}{2kT^2}(\Delta T)^2-\frac{1}{2kT}\left(\frac{\partial\mu}{\partial N}\right)_{V,T}(\Delta N)^2\right) \tag{11.25}$$

$$\langle(\Delta T)^2\rangle=\frac{\int_{-\infty}^{+\infty}(\Delta T)^2\exp\left(-\frac{C_V}{2kT^2}(\Delta T)^2\right)\mathrm{d}(\Delta T)}{\int_{-\infty}^{+\infty}\exp\left(-\frac{C_V}{2kT^2}(\Delta T)^2\right)\mathrm{d}(\Delta T)}=\frac{kT^2}{C_V} \tag{11.26}$$

$$\langle(\Delta N)^2\rangle=\frac{\int_{-\infty}^{+\infty}(\Delta N)^2\exp\left(-\frac{1}{2kT}\left(\frac{\partial\mu}{\partial N}\right)_{V,T}(\Delta N)^2\right)\mathrm{d}(\Delta N)}{\int_{-\infty}^{+\infty}\exp\left(-\frac{1}{2kT}\left(\frac{\partial\mu}{\partial N}\right)_{V,T}(\Delta N)^2\right)\mathrm{d}(\Delta N)}=kT\left(\frac{\partial N}{\partial\mu}\right)_{V,T} \tag{11.27}$$

$$\langle\Delta T\Delta N\rangle=0 \tag{11.28}$$

(3) E 涨落：令 V 不变

$$\Delta E=C_V\Delta T+\left(\frac{\partial E}{\partial N}\right)_{V,T}\Delta N \tag{11.29}$$

$$\begin{aligned}\langle(\Delta E)^2\rangle&=C_V^2\langle(\Delta T)^2\rangle+2C_V\left(\frac{\partial E}{\partial N}\right)_{V,T}\langle\Delta T\Delta N\rangle+\left(\frac{\partial E}{\partial N}\right)_{V,T}^2\langle(\Delta N)^2\rangle\\&=kT^2C_V+kT\left(\frac{\partial N}{\partial\mu}\right)_{V,T}\left(\frac{\partial E}{\partial N}\right)_{V,T}^2\end{aligned} \tag{11.30}$$

11.2 Brown 运动理论

1. Langevin 方程：

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = -\alpha v + F(t) \tag{11.31}$$

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = -\frac{1}{\tau}\frac{\mathrm{d}x}{\mathrm{d}t} + f(t), \quad \frac{1}{\tau} = \frac{\alpha}{m}, \quad f(t) = \frac{F(t)}{m} \tag{11.32}$$

(1) 两边乘 x：

$$\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}x^2 - \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 = -\frac{1}{2\tau}\frac{\mathrm{d}}{\mathrm{d}t}x^2 + xf(t) \tag{11.33}$$

(2) 取系综平均：

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\left\langle x^2\right\rangle + \frac{1}{\tau}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle x^2\right\rangle - \frac{2kT}{m} = 0 \tag{11.34}$$

(3) 通解：

$$\left\langle x^2\right\rangle = \frac{2kT}{\alpha}t + C_1\mathrm{e}^{-t/\tau} + C_2 \tag{11.35}$$

(4) 令 $x(0) = 0,\ t \to +\infty$ ：

$$\left\langle x^2\right\rangle = \frac{2kT}{\alpha}t \tag{11.36}$$

2. Brown 粒子的扩散：

$$\boldsymbol{J} = -D\nabla n, \quad \frac{\partial n}{\partial t} + \nabla\cdot\boldsymbol{J} = 0 \tag{11.37}$$

(1) 扩散方程：

$$\frac{\partial n}{\partial t} - D\frac{\partial^2 n}{\partial x^2} = 0 \tag{11.38}$$

(2) 初始条件：

$$n(x,0) = N\delta(x) \tag{11.39}$$

(3) 粒子的密度分布：

$$n(x,t) = \frac{N}{\sqrt{4\pi Dt}}\mathrm{e}^{-\frac{x^2}{4Dt}} \tag{11.40}$$

(4) 粒子的位移方均：

$$\left\langle x^2\right\rangle = \frac{1}{N}\int_{-\infty}^{+\infty} x^2 n(x,t)\mathrm{d}x = 2Dt \tag{11.41}$$

(5) Einstein 关系：

$$D = \frac{kT}{\alpha} \tag{11.42}$$

3. 无规行走：

(1) 走 N 步后的位移：

$$x = (N_+ - N_-)\lambda = m\lambda, \quad N = \frac{t}{\tau} \tag{11.43}$$

(2) 走 N 步的走法数：

$$\sum_{N_+=0}^{N}\frac{N!}{N_+!(N-N_+)!} = (1+1)^N = 2^N \tag{11.44}$$

(3) 位移为 x 的概率：

$$P_N(m) = \frac{N!}{N_+!(N-N_+)!}\left(\frac{1}{2}\right)^N = \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!}\left(\frac{1}{2}\right)^N = \sqrt{\frac{2}{\pi N}}\mathrm{e}^{-\frac{m^2}{2N}} \tag{11.45}$$

$$P(x,t)\mathrm{d}x = P_N(m)\frac{\mathrm{d}x}{2\lambda} = \frac{1}{\sqrt{4\pi Dt}}\mathrm{e}^{-\frac{x^2}{4Dt}}\mathrm{d}x, \quad D = \frac{\lambda^2}{2\tau} \tag{11.46}$$

(4) 粒子的位移方均：

$$\left\langle x^2\right\rangle = \frac{1}{N}\int_{-\infty}^{+\infty} x^2 P(x,t)\mathrm{d}x = 2Dt \tag{11.47}$$

12 非平衡态统计理论

12.1 Boltzmann 积分微分方程

1. 非平衡态分布函数:

$$\mathrm{d}N(\boldsymbol{r},\boldsymbol{v},t)=f(\boldsymbol{r},\boldsymbol{v},t)\mathrm{d}^3r\mathrm{d}^3v \tag{12.1}$$

2. 分布函数变化率:

$$(f(\boldsymbol{r},\boldsymbol{v},t+\mathrm{d}t)-f(\boldsymbol{r},\boldsymbol{v},t))\mathrm{d}^3r\mathrm{d}^3v=\frac{\partial f}{\partial t}\mathrm{d}t\mathrm{d}^3r\mathrm{d}^3v \tag{12.2}$$

$$\frac{\partial f}{\partial t}=\left(\frac{\partial f}{\partial t}\right)_d+\left(\frac{\partial f}{\partial t}\right)_c \tag{12.3}$$

3. 漂移项:

$$\begin{aligned}\left(\frac{\partial f}{\partial t}\right)_d&=-\left(\frac{\partial(\dot{x}f)}{\partial x}+\frac{\partial(\dot{y}f)}{\partial y}+\frac{\partial(\dot{z}f)}{\partial z}+\frac{\partial(\dot{v}_xf)}{\partial v_x}+\frac{\partial(\dot{v}_yf)}{\partial v_y}+\frac{\partial(\dot{v}_zf)}{\partial v_z}\right)\\&=-\left(v_x\frac{\partial f}{\partial x}+v_y\frac{\partial f}{\partial y}+v_z\frac{\partial f}{\partial z}+a_x\frac{\partial f}{\partial v_x}+a_y\frac{\partial f}{\partial v_y}+a_z\frac{\partial f}{\partial v_z}\right)\\&=-(\boldsymbol{v}\cdot\nabla_rf+\boldsymbol{a}\cdot\nabla_vf)\end{aligned} \tag{12.4}$$

4. 碰撞项:

(1) 能动量守恒:

$$m_1\boldsymbol{v}_1+m_2\boldsymbol{v}_2=m_1\boldsymbol{v}_1'+m_2\boldsymbol{v}_2' \tag{12.5}$$

$$\frac{1}{2}m_1\boldsymbol{v}_1^2+\frac{1}{2}m_2\boldsymbol{v}_2^2=\frac{1}{2}m_1{\boldsymbol{v}_1'}^2+\frac{1}{2}m_2{\boldsymbol{v}_2'}^2 \tag{12.6}$$

$$\boldsymbol{v}_1'-\boldsymbol{v}_1=\lambda_1\boldsymbol{n},\quad \boldsymbol{v}_2'-\boldsymbol{v}_2=\lambda_2\boldsymbol{n} \tag{12.7}$$

(2) 碰后速度:

$$\boldsymbol{v}_1'=\boldsymbol{v}_1+\frac{2m_2}{m_1+m_2}[(\boldsymbol{v}_2-\boldsymbol{v}_1)\cdot\boldsymbol{n}]\boldsymbol{n} \tag{12.8}$$

$$\boldsymbol{v}_2'=\boldsymbol{v}_2+\frac{2m_1}{m_1+m_2}[(\boldsymbol{v}_2-\boldsymbol{v}_1)\cdot\boldsymbol{n}]\boldsymbol{n} \tag{12.9}$$

(3) 反碰撞项:

$$(\boldsymbol{v}_2'-\boldsymbol{v}_1')^2=(\boldsymbol{v}_2-\boldsymbol{v}_1)^2,\quad (\boldsymbol{v}_1'-\boldsymbol{v}_2')\cdot(-\boldsymbol{n})=(\boldsymbol{v}_1-\boldsymbol{v}_2)\cdot\boldsymbol{n} \tag{12.10}$$

(4) 元碰撞数:

$$(f_1\mathrm{d}^3r\mathrm{d}^3v_1)\cdot(f_2\mathrm{d}^3v_2)\cdot d_{12}^2\mathrm{d}\varOmega\cdot(\boldsymbol{v}_1-\boldsymbol{v}_2)\cdot\boldsymbol{n}\mathrm{d}t,\quad \varLambda_{12}=d_{12}^2(\boldsymbol{v}_1-\boldsymbol{v}_2)\cdot\boldsymbol{n} \tag{12.11}$$

$$\varLambda_{12}'=\varLambda_{12},\quad \mathrm{d}\varOmega'=\mathrm{d}\varOmega,\quad \mathrm{d}^3v_1'\mathrm{d}^3v_2'=|J|\mathrm{d}^3v_1\mathrm{d}^2v_2=\mathrm{d}^3v_1\mathrm{d}^2v_2 \tag{12.12}$$

$$\delta N_1^{(-)}=f_1f_2\mathrm{d}^3v_1\mathrm{d}^3v_2\varLambda_{12}\mathrm{d}\varOmega\mathrm{d}t\mathrm{d}^3r \tag{12.13}$$

$$\delta N_1^{(+)}=f_1'f_2'\mathrm{d}^3v_1\mathrm{d}^3v_2\varLambda_{12}\mathrm{d}\varOmega\mathrm{d}t\mathrm{d}^3r \tag{12.14}$$

(5) 碰撞项:

$$\left(\frac{\partial f}{\partial t}\right)_c\mathrm{d}t\mathrm{d}^3r\mathrm{d}^3v_1=\Delta N_1^{(+)}-\Delta N_1^{(-)}=\left[\int(f_1'f_2'-f_1f_2)\mathrm{d}^3v_2\varLambda\mathrm{d}\varOmega\right]\mathrm{d}t\mathrm{d}^3r\mathrm{d}^3v_1 \tag{12.15}$$

5. Boltzmann 积分微分方程:

$$\frac{\partial f}{\partial t}+\boldsymbol{v}\cdot\nabla_rf+\boldsymbol{a}\cdot\nabla_vf=\int(f_1'f_2'-f_1f_1)\mathrm{d}^3v_2\varLambda\mathrm{d}\varOmega \tag{12.16}$$

12.2 H 定理

1. H 函数:

$$H=\int f(\boldsymbol{r},\boldsymbol{v},t)\ln f(\boldsymbol{r},\boldsymbol{v},t)\mathrm{d}^3r\mathrm{d}^3v \tag{12.17}$$

2. H 函数的变化:

$$\begin{aligned}\frac{\mathrm{d}H}{\mathrm{d}t}&=\int\left(\frac{\partial f_1}{\partial t}\ln f_1+\frac{\partial f_1}{\partial t}\right)\mathrm{d}^3r\mathrm{d}^3v_1=\int(1+\ln f_1)\frac{\partial f_1}{\partial t}\mathrm{d}^3r\mathrm{d}^3v_1 &(12.18)\\&=-\int(1+\ln f_1)\left(\boldsymbol{v}_1\cdot\nabla_r f_1\right)\mathrm{d}^3r\mathrm{d}^3v_1\\&\quad-\int(1+\ln f_1)\left(\boldsymbol{a}\cdot\nabla_v f_1\right)\mathrm{d}^3r\mathrm{d}^3v_1\\&\quad-\int(1+\ln f_1)(f_1f_2-f_1'f_2')\mathrm{d}^3r\mathrm{d}^3v_1\mathrm{d}^3v_2\Lambda\mathrm{d}\Omega &(12.19)\end{aligned}$$

(1) 第一项:

$$\int(1+\ln f_1)\left(\boldsymbol{v}_1\cdot\nabla_r f_1\right)\mathrm{d}^3r=\int\nabla_r\cdot(\boldsymbol{v}_1f_1\ln f_1)\mathrm{d}^3r=\oint\boldsymbol{n}\cdot(\boldsymbol{v}_1\ln f_1)\mathrm{d}\sigma=0 \tag{12.20}$$

(2) 第二项:

$$\int(1+\ln f_1)a_x\frac{\partial f_1}{\partial v_x}\mathrm{d}v_x=\int\frac{\partial}{\partial v_x}(a_xf_1\ln f_1)\mathrm{d}v_x=\Big[a_xf_1\ln f_1\Big]_{-\infty}^{+\infty}=0 \tag{12.21}$$

(3) 第三项:

$$\frac{\mathrm{d}H}{\mathrm{d}t}=-\frac{1}{4}\int[\ln(f_1f_2)-\ln(f_1'f_2')](f_1f_2-f_1'f_2')\mathrm{d}^3r\mathrm{d}^3v_1\mathrm{d}^3v_2\Lambda\mathrm{d}\Omega \tag{12.22}$$

3. H 定理:

$$\frac{\mathrm{d}H}{\mathrm{d}t}\leqslant 0,\quad\text{当且仅当 } f_1f_2=f_1'f_2' \text{ 时等号成立} \tag{12.23}$$

4. 细致平衡:

$$f_1f_2=f_1'f_2' \tag{12.24}$$

12.3 平衡态分布函数

1. 细致平衡:

$$\ln f_1+\ln f_2=\ln f_1'+\ln f_2' \tag{12.25}$$

2. 通解:

$$\ln f=\alpha_0+\boldsymbol{\alpha}\cdot m\boldsymbol{v}+\alpha_4\frac{1}{2}m\boldsymbol{v}^2 \tag{12.26}$$

3. 平衡态分布函数的形式:

$$f=n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\mathrm{e}^{-\frac{m}{2kT}(\boldsymbol{v}-\boldsymbol{v}_0)^2} \tag{12.27}$$

4. 平衡态分布函数的参数确定:

$$\boldsymbol{v}\cdot\nabla_r\left[\ln n+\frac{3}{2}\ln\frac{m}{2\pi kT}-\frac{m}{2kT}(\boldsymbol{v}-\boldsymbol{v}_0)^2\right]-\frac{m}{kT}\boldsymbol{a}\cdot(\boldsymbol{v}-\boldsymbol{v}_0)=0 \tag{12.28}$$

(1) $\boldsymbol{v}^3$ 系数:

$$\nabla_rT=0\Rightarrow\frac{\partial T}{\partial x}=\frac{\partial T}{\partial y}=\frac{\partial T}{\partial z}=0 \tag{12.29}$$

(2) $\boldsymbol{v}^2$ 系数:

$$\boldsymbol{v}\cdot\nabla(\boldsymbol{v}\cdot\boldsymbol{v}_0)=0\Rightarrow\boldsymbol{v}_0=\boldsymbol{v}_c+\boldsymbol{\omega}\times\boldsymbol{r} \tag{12.30}$$

(3) $\boldsymbol{v}^1$ 系数:

$$\nabla_r\left(\ln n-\frac{m}{2kT}\boldsymbol{v}_0^2\right)-\frac{m}{kT}\boldsymbol{a}=0\Rightarrow n=n_0\mathrm{e}^{\frac{m}{2kT}\boldsymbol{v}_0^2-\frac{m}{kT}\varphi(\boldsymbol{r})} \tag{12.31}$$

(4) $\boldsymbol{v}^0$ 系数:

$$\boldsymbol{a}\cdot\boldsymbol{v}_0=0 \tag{12.32}$$

12.4 Boltzmann 方程的弛豫时间近似

1. 局域平衡分布函数:

$$f^{(0)}(\boldsymbol{r},\boldsymbol{v},t)=n(\boldsymbol{r},t)\left(\frac{m}{2\pi kT(\boldsymbol{r},t)}\right)^{\frac{3}{2}}\mathrm{e}^{-\frac{m}{2kT(\boldsymbol{r},t)}(\boldsymbol{v}-\boldsymbol{v}_0(\boldsymbol{r},t))^2} \tag{12.33}$$

2. 弛豫时间近似:

$$\left[\frac{\partial}{\partial t}(f-f^{(0)})\right]_c=-\frac{f-f^{(0)}}{\tau} \tag{12.34}$$

$$f(t)=f^{(0)}=[f(0)-f^{(0)}]\mathrm{e}^{-t/\tau} \tag{12.35}$$

3. Boltzmann 方程的弛豫时间近似:

$$\frac{\partial f}{\partial t}+\boldsymbol{v}\cdot\nabla_r f+\boldsymbol{a}\cdot\nabla_v f=-\frac{f-f^{(0)}}{\tau} \tag{12.36}$$

12.5 气体的黏滞定律

1. Newton 黏滞定律:

$$F_{xy}=\eta\frac{\mathrm{d}v_0}{\mathrm{d}x} \tag{12.37}$$

2. 动量传递:

$$F_{xy}=\frac{\mathrm{d}p}{\mathrm{d}t\mathrm{d}y\mathrm{d}z}=-\int_{-\infty}^{+\infty}mv_y\cdot v_x f\mathrm{d}^3v \tag{12.38}$$

3. 局域平衡分布函数:

$$f^{(0)}=n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\mathrm{e}^{-\frac{m}{2kT}(v_x^2+(v_y-v_0)^2+v_z^2)} \tag{12.39}$$

4. 局域非平衡分布函数:

$$v_x\frac{\partial f}{\partial x}=-\frac{f-f^{(0)}}{\tau} \tag{12.40}$$

$$f\approx f^{(0)}+f^{(1)}=f^{(0)}+\tau v_x\frac{\partial f^{(0)}}{\partial v_y}\frac{\mathrm{d}v_0}{\mathrm{d}x} \tag{12.41}$$

5. 黏度:

$$F_{xy}=-m\frac{\mathrm{d}v_0}{\mathrm{d}x}\int_{-\infty}^{+\infty}v_x^2v_y\tau\frac{\partial f^{(0)}}{\partial v_y}\mathrm{d}^3v=m\langle\tau\rangle\frac{\mathrm{d}v_0}{\mathrm{d}x}\int_{-\infty}^{+\infty}v_x^2f^{(0)}\mathrm{d}^3v=nm\langle\tau\rangle\langle v_x^2\rangle\frac{\mathrm{d}v_0}{\mathrm{d}x} \tag{12.42}$$

$$\eta=nm\langle\tau\rangle\langle v_x^2\rangle=nkT\langle\tau\rangle \tag{12.43}$$

12.6 金属的 Ohm 定律

1. Ohm 定律:

$$J_z=\sigma_z E_z \tag{12.44}$$

2. 电流密度:

$$J_z=-e\int fv_z\frac{2m^3\mathrm{d}^3v}{h^3} \tag{12.45}$$

3. 局域平衡分布函数:

$$f^{(0)}=\frac{1}{\mathrm{e}^{\beta(\frac{p^2}{2m}-\mu)}+1} \tag{12.46}$$

4. 局域非平衡分布函数:

$$-\frac{eE_z}{m}\frac{\partial f}{\partial v_z}=-\frac{f-f^{(0)}}{\tau} \tag{12.47}$$

$$f\approx f^{(0)}+f^{(1)}=f^{(0)}+\frac{eE_z}{m}\tau\frac{\partial f^{(0)}}{\partial v_z} \tag{12.48}$$

5. 电导率:

$$J_z = -\frac{e^2E_z}{m}\int_{-\infty}^{+\infty}\tau v_z\frac{\partial f^{(0)}}{\partial v_z}\frac{2m^3\mathrm{d}^3v}{h^3} = -\frac{e^2E_z}{m}\tau_F\int_{-\infty}^{+\infty}v_z\frac{\partial f^{(0)}}{\partial v_z}\frac{2m^3\mathrm{d}^3v}{h^3}$$
$$= \frac{e^2E_z}{m}\tau_F\int_{-\infty}^{+\infty}f^{(0)}\frac{2m^3\mathrm{d}^3v}{h^3} = \frac{ne^2\tau_F}{m}E_z \tag{12.49}$$

$$\sigma = \frac{ne^2\tau_F}{m} \tag{12.50}$$