# 平衡态统计物理
# 复习

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2017年11月20日

## 1 热力学定律

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

$$\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V \tag{2}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{3}$$

$$S = nC_p lnT - nRlnp + S_0 \Rightarrow \Delta S = C_p ln\frac{T_2}{T_1} \tag{4}$$

$$S = nC_V lnT + nRlnV + S_0 \Rightarrow \Delta S = C_V ln\frac{T_2}{T_1} \tag{5}$$

$$p = \frac{RT}{V_m - b} - \frac{a}{V_M^2} \tag{6}$$

$$dW = \sigma dA \tag{7}$$

声速

$$a = \sqrt{\frac{dp}{d\rho}} \tag{8}$$

$$a^2 = \left(\frac{\partial p}{\partial \rho}\right)_S = -v^2\left(\frac{\partial p}{\partial v}\right)_S \tag{9}$$

$$= \gamma p v \tag{10}$$

# 2 自由能

## 2.1 原型

$$U = TS - PV + \mu N \tag{11}$$
$$H = U + PV \tag{12}$$
$$F = U - TS \tag{13}$$
$$G = U - TS + PV \tag{14}$$
$$\Omega = U - TS - \mu N \tag{15}$$

## 2.2 电

$$\varepsilon(T) = \frac{D}{E} \tag{16}$$
$$dW = VEdD \tag{17}$$
$$p \to -E, V \to VD \tag{18}$$

## 2.3 磁

## 2.4 微分形式

$$dU = TdS + \Sigma Y_i dy_i + \mu dN \tag{19}$$
$$dH = TdS + Vdp + \mu dN \tag{20}$$
$$dF = -SdT - PdV + \mu dN \tag{21}$$
$$dG = -SdT + Vdp + \mu dN \tag{22}$$
$$d\Omega = -SdT - PdV - Nd\mu \tag{23}$$
$$Nd\mu = -SdT + Vdp \tag{24}$$

# 3 麦克斯韦关系

## 3.1 经典

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \left(\frac{\partial T}{\partial N}\right)_T = -\left(\frac{\partial \mu}{\partial S}\right)_N, \left(\frac{\partial p}{\partial N}\right)_{T,N} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,V} \tag{25}$$

## 3.2 扩展

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)\left(\frac{\partial V}{\partial T}\right) \tag{26}$$

$$= \frac{VT}{\kappa_T}\alpha^2 \tag{27}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{28}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{29}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{30}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{31}$$

$$\tag{32}$$

吉布斯-亥姆霍兹方程

$$U = F - T\left(\frac{\partial F}{\partial T}\right) = G - T\left(\frac{\partial G}{\partial T}\right) - p\left(\frac{\partial G}{\partial p}\right) \tag{33}$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right) \tag{34}$$

# 4 普朗克

$$Q = \sigma T^4 \tag{35}$$

# 5 热力学平衡条件

$$\delta^2 S = -\frac{C_V}{T^2}(\delta T)^2 + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)(\delta V)^2 \tag{36}$$

$$\Delta S < 0, \Delta U > 0, \Delta H > 0, \Delta F > 0, \Delta G > 0 \tag{37}$$

# 6 相平衡

$$Clapeyron\ equation: \frac{dp}{dT} = \frac{L}{T(V_m^\beta - V_m^\alpha)} \tag{38}$$

斯特林公式:

$$lnN! = NlnN - N \tag{39}$$

相平衡共存

$$\text{热平衡条件：} T^\alpha = T^\beta = T \qquad program@eps$$

$$\text{力学平衡条件：} p^\alpha = p^\beta = p \qquad program@eps$$

$$\text{相变平衡条件：} \mu^\alpha(T,p) = \mu^\beta(T,p) \qquad program@eps$$

# 7 系综

## 7.1 欧拉定理

欧拉定理:

$$if: f(\lambda x_1, \ldots, \lambda x_k) = \lambda^m f(x^1, \ldots, x_k) \tag{43}$$

$$then: \Sigma_i x_i \frac{\partial f}{\partial x_i} = mf \tag{44}$$

### 7.2 溶液蒸发点

$$g' = g + RTln(1-x) \tag{45}$$

### 7.3 熵

$$S = -k\Sigma_s \rho_s ln\rho_s, \rho_s = \begin{cases} \frac{1}{\Omega} & \text{微正则} \\ \frac{1}{Z}e^{-\beta E_s} & \text{正则} \\ \frac{1}{\Xi}e^{-\alpha N - \beta E_s} \end{cases} \tag{46}$$

### 7.4 配分方程

#### 7.4.1 正则(T,V,N)

$$Z = \frac{1}{N!h^{3N}}\int s^{-\beta E} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N} \tag{47}$$

$$\beta = \frac{1}{kT} \tag{48}$$

$$\rho_s = \frac{1}{Z}e^{-\beta E_s} \tag{49}$$

$$U = -\frac{\partial}{\partial \beta} lnZ \tag{50}$$

$$Y = -\frac{1}{\beta}\frac{\partial}{\partial y} lnZ \tag{51}$$

$$F = -kTlnZ \tag{52}$$

$$S = k(lnZ - \beta\frac{\partial}{\partial \beta} lnZ) \tag{53}$$

$$\mu = -kT\frac{\partial}{\partial N} lnZ \tag{54}$$

$$\overline{(E-\bar{E})^2} = -\frac{\partial E}{\partial \beta} = kT^2 C_V \tag{55}$$

#### 7.4.2 微正则（E,V,N)

$$\rho_s = \frac{1}{\Omega} \tag{56}$$

$$\Omega = \frac{1}{\prod_i N_i! h^{N_i r}} \int_{E \leq H(q,p) \leq E+\delta E} d\Omega \tag{57}$$

$$\alpha = \left(\frac{\partial ln\Omega_r}{\partial N_r}\right) = -\frac{\mu}{kT} \tag{58}$$

$$\beta = \left(\frac{\partial ln\Omega_r}{\partial E_r}\right) = \frac{1}{kT} \tag{59}$$

$$S(N,E,V) = kln\Omega(N,E,V) \tag{60}$$

$$dS = \frac{1}{T}(pdV - \mu dN) \tag{61}$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \tag{62}$$

$$p = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \tag{63}$$

$p, \mu$都可以通过偏导求出。

### 7.5 巨正则（$\mu$,E,V）

$$\Xi = \Sigma_{N=0}^{\infty}\Sigma_s e^{-\alpha N-\beta E} \tag{64}$$

$$= \Sigma_N \frac{e^{-\alpha N}}{N!h^{Nr}}\int e^{-\beta E(q,p)}d\Omega \tag{65}$$

$$\rho_{Ns} = \frac{1}{\Xi}e^{-\alpha V-\beta E_s} \tag{66}$$

$$\bar{N} = -\frac{\partial}{\partial\alpha}ln\Xi \tag{67}$$

$$U = -\frac{\partial}{\partial\beta}ln\Xi \tag{68}$$

$$p = \frac{1}{\beta}\frac{\partial}{\partial V}ln\Xi \tag{69}$$

$$Y = -\frac{1}{\beta}\frac{\partial}{\partial y}ln\Xi \tag{70}$$

$$S = k(ln\Xi - \alpha\frac{\partial}{\partial\alpha}ln\Xi - \beta\frac{\partial}{\partial\beta}ln\Xi) \tag{71}$$

$$\overline{(N-\bar{N})^2} = kT\left(\frac{\partial\bar{N}}{\partial\mu}\right)_{T,N} \tag{72}$$

$$= \frac{kT}{V}\kappa_T \tag{73}$$

# 8 涨落

$$W \propto e^{-\frac{\Delta S\Delta T-\Delta p\Delta V}{2kT}} \tag{74}$$

$$\overline{\Delta T\cdot\Delta V} = \overline{\Delta T}\cdot\overline{\Delta V} = 0 \tag{75}$$

$$\overline{(\Delta T)^2} = \frac{kT^2}{C_V} \tag{76}$$

$$\overline{(\Delta V)^2} = -kT\left(\frac{\partial V}{\partial p}\right)_T \tag{77}$$

巨正则系综涨落

$$W \propto e^{-\frac{\Delta S\Delta T-\Delta p\Delta V+\Delta\mu\Delta N}{2kT}} \tag{78}$$

高斯分布

$$P(n) = \frac{1}{\sqrt{2\pi(\Delta n)^2}} e^{-\frac{(n-\bar{n})^2}{2(\Delta n)^2}} \tag{79}$$

# 9 蛋变鸡

鸡作为一个生物体并没有处在平衡态，因此不好用平常的方法衡量其熵的大小。然而我们考虑鸡蛋的混乱程度，其显然比鸡的混乱程度更大。