Review

什么是热力学？

宏观物体是由大量微观粒子（分子或其它粒子）构成的。

这些微观粒子不停地进行无规则地运动。

人们把这大量微观粒子的无规则运动称为物质的热运动。

热运动有其自身固有的规律性。热力学的任务是研究热运动的规律及热运动对物质宏观性质的影响。

热力学是热运动的宏观理论

热力学理论的普适性

通过对热现象的观测、实验和分析，人们总结出热现象的基本规律，这就是热力学第一定律、第二定律和第三定律。这几个基本定律是无数经验的总结，适用于一切物质系统。这就是说，它们具有高度的可靠性和普遍性。热力学以这几个基本定律为基础，应用数学方法，通过逻辑演绎可以得到有关物质各种宏观性质之间的关系、宏观物理过程进行的方向和限度等结论。只要在其中不加其它假设，这些结论就具有同样的可靠性和普遍性。普遍性是热力学方法的优点。我们可以应用热力学理论研究一切宏观物质系统。

A theory is the more impressive the greater the simplicity of its premises, the more deferent kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.
. . . . *A. Einstein*
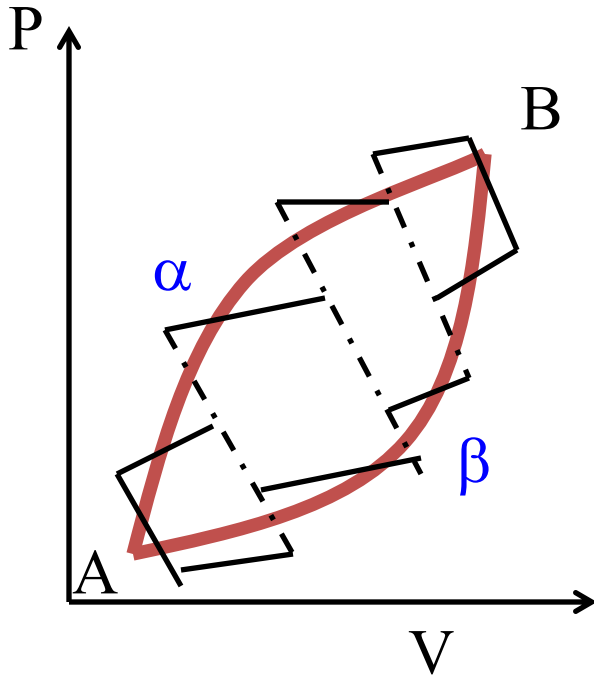
热力学第二定律（1）

The First Law: the conservation of energy and energy transfer in terms of heat and work.   Energy is a state function.

The Second Law: ENTROPY.

The first law places no limits on the amounts that can be converted.
The second law is concerned with limits on the conversion of "heat" into "work" by heat engines.

$$\frac{\delta Q_{rev}}{T} = dS$$

Entropy as a State Function(3)

$$\oint \frac{\delta Q_r}{T} = \int\limits_A^B \left(\frac{\delta Q_r}{T} \right)_\alpha + \int\limits_B^A \left(\frac{\delta Q_r}{T} \right)_\beta = 0$$

$$\int\limits_A^B \left(\frac{\delta Q_r}{T} \right)_\alpha = -\int\limits_B^A \left(\frac{\delta Q_r}{T} \right)_\beta = \int\limits_A^B \left(\frac{\delta Q_r}{T} \right)_\beta$$

这一积分的数值与积分的途径无关，代表着某个状态的改变量，定义为熵

For a close system the reversible heat flow divided by the absolute temperature of the system is a state or point function.

判断过程的方向

孤立体系 （dU=0，dV=0），熵增原理

$$\left(\Delta S\right)_{U,V} > 0 \quad \text{表示自发}$$

$$\left(\Delta S\right)_{U,V} = 0 \quad \text{表示平衡}$$

$$\left(\Delta S\right)_{U,V} < 0 \quad \text{表示不可能}$$

非孤立体系

$$\Delta S > \Sigma \frac{\delta Q}{T} \quad \text{表示不可逆}$$

$$\Delta S = \Sigma \frac{\delta Q}{T} \quad \text{表示可逆或平衡}$$

$$\Delta S < \Sigma \frac{\delta Q}{T} \quad \text{表示不可能进行}$$

当系统由始态I经过某一过程变到终态II后，如能使系统再回到原态，同时也消除了原过程对环境所产生的一切影响，则原来过程称为可逆过程。

$$H \equiv U + PV$$

$$G \equiv H - TS$$

$$F \equiv U - TS$$

$$dU = TdS - PdV$$

$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$
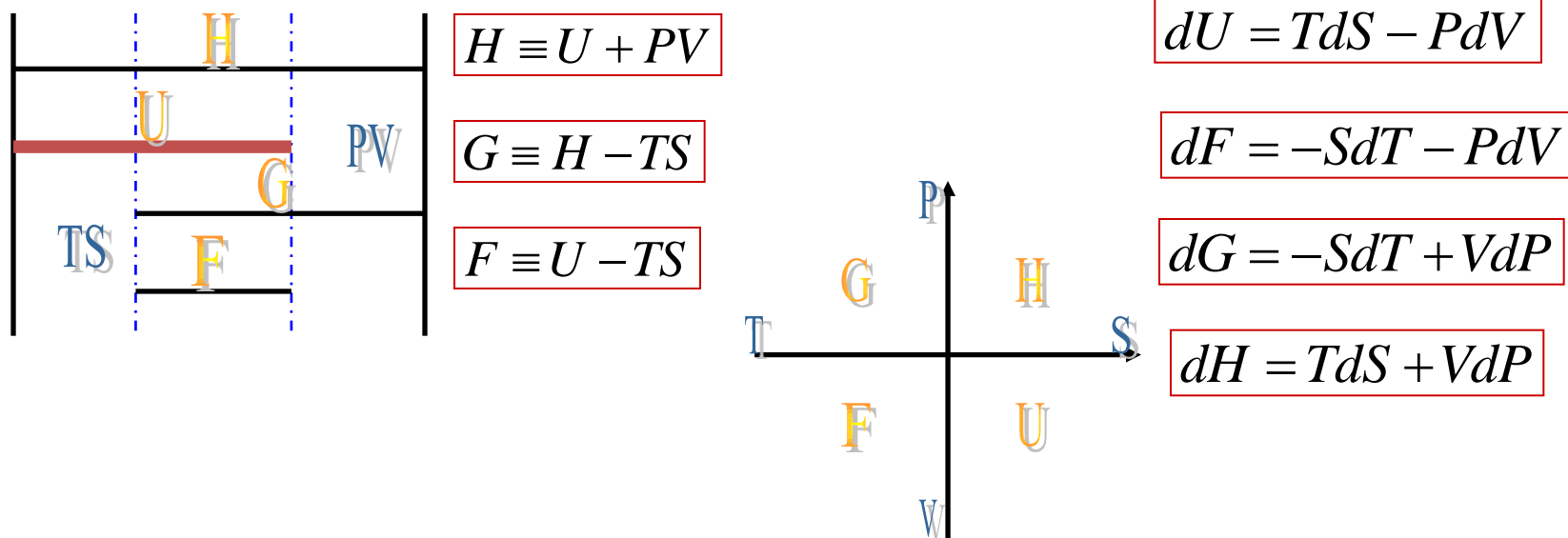
$$dH = TdS + VdP$$

μ_i　The chemical potential of the component i.

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j \neq n_i} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_j \neq n_i} = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j \neq n_i} = \mu_i$$

热力学函数关系（13）

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$

$$dz = Mdx + Ndy$$

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

$$\left(\frac{\partial U}{\partial S} \right)_V = T \qquad \left(\frac{\partial U}{\partial V} \right)_S = -P$$

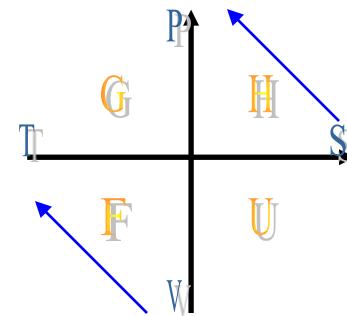$$\left(\frac{\partial F}{\partial T} \right)_V = -S \qquad \left(\frac{\partial F}{\partial V} \right)_T = -P$$

$$\left(\frac{\partial G}{\partial T} \right)_P = -S \qquad \left(\frac{\partial G}{\partial P} \right)_T = V$$

$$\left(\frac{\partial H}{\partial S} \right)_P = T \qquad \left(\frac{\partial H}{\partial P} \right)_S = V$$

$$\left(\frac{\partial T}{\partial V} \right)_S = -\left(\frac{\partial P}{\partial S} \right)_V$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

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

$$-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

多相平衡（2）

- Two states are in equilibrium when no reversible work can be done by having the system change between those two states

$$\delta W_{rev.1 \to 2} = 0$$

- The temperatures in the two states must be equal

  - A consequence of the second law of thermodynamics

多相平衡（3）

$$\left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,2} dn_i - \left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,1} dn_i = \delta W_{rev}$$

Condition of equilibrium $\qquad \delta W_{rev.1\rightarrow 2} = 0$

$$\left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,2} dn_i = \left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,1} dn_i$$

At the same potential energy level and kinetic level

$$\left(\overline{G}_{i,2} - \overline{G}_{i,1}\right) dn_i = \Delta \overline{G}_i = 0 \qquad \overline{G}_{i,2} = \overline{G}_{i,1}$$

$$\mu_{i,2} = \mu_{i,1}$$

In term of the chemical potential of i

Enthalpy of Mixing: Ideal Solution (1)

The enthalpy of mixing of a solution,

$$\frac{d\left(\dfrac{\overline{G}_A^{rel}}{T}\right)}{d\left(\dfrac{1}{T}\right)} = \overline{H}_A^{rel} \quad \Longleftarrow \quad d\left(\frac{\Delta G}{T}\right)_P = \Delta H d\left(\frac{1}{T}\right)_P$$
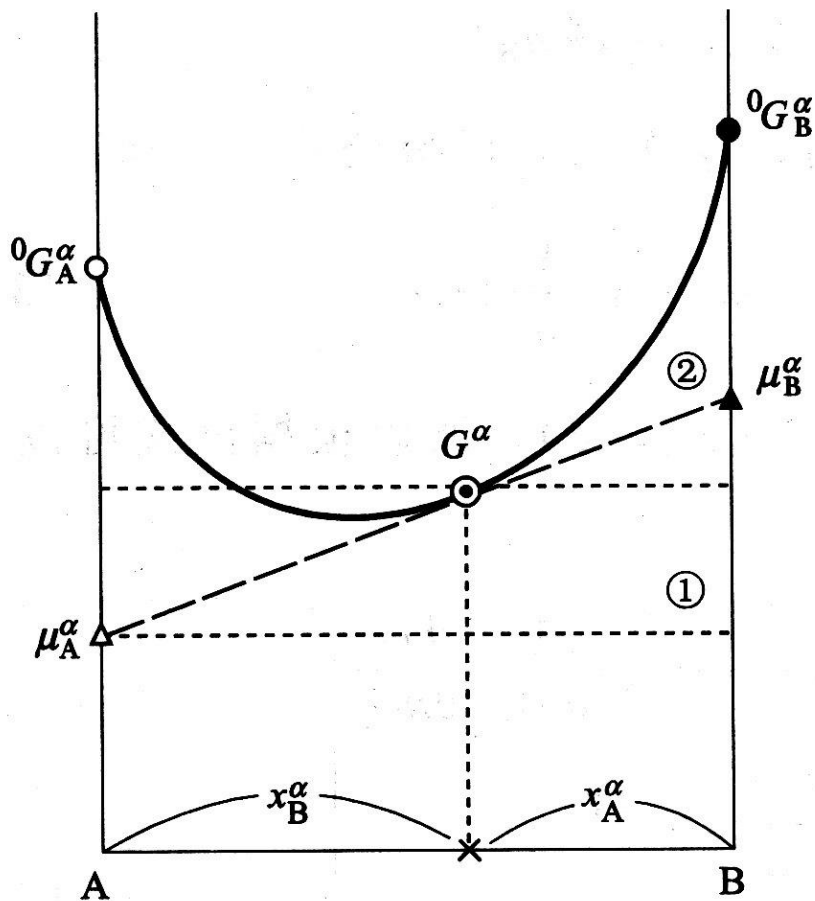
For an ideal solution: $\overline{G}_A^{rel} = RT \ln \alpha_A = RT \ln x_A$

$$\frac{d(R \ln x_A)}{dT} = \overline{H}_A^{rel} = 0 = \overline{H}_A - \underline{H}_A$$

The enthalpy of mixing of an ideal solution is zero:

$$\underline{H}_M = x_A \overline{H}_A^{rel} + x_B \overline{H}_B^{rel} = 0 \qquad \text{(ideal solution)}$$

Binary

(a) A-B系

A-B二元自由能和化学势之间的关系

$$G^\alpha = \mu_A^\alpha \cdot x_A + \mu_B^\alpha \cdot x_B$$

$$\mu_A^\alpha = G^\alpha - \left(\frac{\partial G^\alpha}{\partial x_B}\right) \cdot x_B$$

$$\mu_B^\alpha = G^\alpha - \left(\frac{\partial G^\alpha}{\partial x_B}\right) \cdot x_B + \left(\frac{\partial G^\alpha}{\partial x_B}\right)$$

Ternay
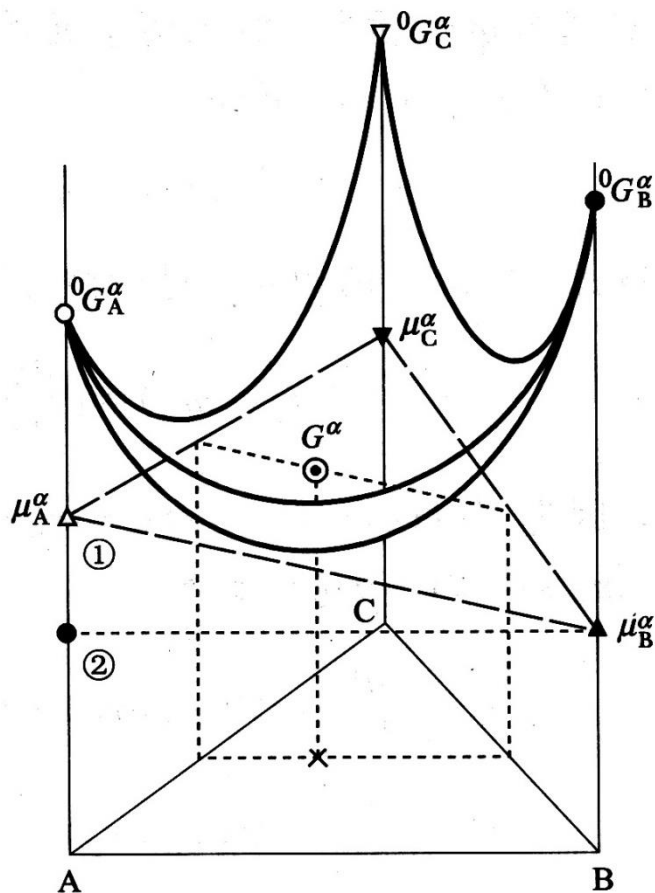
(b) A-B-C系

A-B-C三元系自由能和化学势之间的关系

$$\mu_1^\alpha = G^\alpha - \sum_{i=2}^{n} \left(\frac{\partial G^\alpha}{\partial x_i}\right) \cdot x_i$$

$$\mu_j^\alpha = \mu_1^\alpha + \left(\frac{\partial G^\alpha}{\partial x_j}\right)$$

$$G^\alpha = \sum_{i=1}^{n} \mu_i^\alpha \cdot x_i = \mu_1^\alpha + \sum_{i=2}^{n} (\mu_i^\alpha - \mu_1^\alpha) \cdot x_i$$

$$\mu_i^\alpha - \mu_1^\alpha = \left(\frac{\partial G^\alpha}{\partial x_i}\right)$$

稀溶液及其依数性

- 稀溶液

溶剂符合Raoult定量，即理想溶液

溶质符合Henry定量，非理想，活度系数为常数

Raoult's law and Henry's law

Raoult's law
1887年，经验定律，

$$P_A = P_A^* x_A \Rightarrow a_A = x_A$$

"溶液中溶剂的蒸气压P_A等于同一温度下纯溶剂的蒸气压
P^*_A与溶液中溶剂的摩尔分数x_A的乘积"

Henry's law
1803年，经验定律

$$x_B = k'_{x,B} P_B \Rightarrow P_B = k_{x,B} x_B \not\Rightarrow \gamma_B = 1$$

$$k_{x,B} ? P_B^*$$

"在一定温度下微溶气体在溶液中的平衡组成与该气体的
平衡气相分压成正比"

Regular Solution (3)

For the regular solution: $\underline{S}^{xs}{}_M = 0$ $\underline{G}^{xs}_M = \underline{H}^{xs}_M = \omega x_A x_B$

$$\overline{H}^{xs}_B = \underline{H}^{xs}_M + x_A\left(\frac{\partial \underline{H}^{xs}_M}{\partial x_B}\right)_T$$
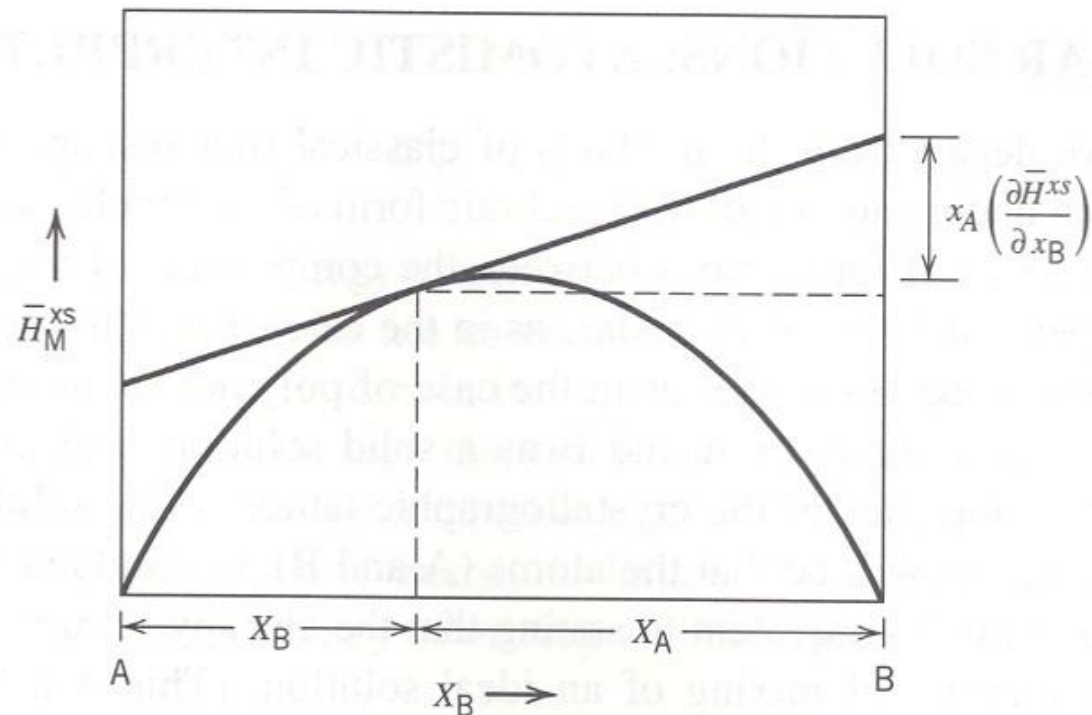
Figure 7.13 Plot of excess enthalpy of mixing versus composition for a nonideal solution.

何谓相：物理、化学性质相同的均匀部分

相与相之间有明确界面，越过界面，性质突变

Decomposition of calcium carbonate into calcium oxide and carbon dioxide

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Nitrogen is added to the system……

Four chemical species and one relationship among them
Components: 3
Three phases, P=3

Meaning of F=2?

$$\boxed{F = C - P + 2 = 3 - 3 + 2 = 2}$$

The temperature and the total pressure can each be varied independently.

Fraction of N_2 or CO_2 in gas phase?

单组分系统

- 相律分析

$$F = C - P + 2$$

$$P \geq 1; F \geq 0$$

$$\boxed{C = 1}$$

$$\begin{array}{l} P = 1, F = 2 \\ P = 2, F = 1 \\ P = 3, F = 0 \end{array}$$

- 物态转变方程式

$$\frac{dP}{dT} = \frac{\Delta_\alpha^\beta \underline{H}}{T \Delta_\alpha^\beta \underline{V}}$$

$$P = A \exp\left(-\frac{\Delta_\alpha^\beta \underline{H}}{RT} \right)$$

$$\Delta P = \frac{\Delta_\alpha^\beta \underline{H}}{\Delta_\alpha^\beta \underline{V}} \frac{\Delta T}{T_1} = K \cdot \Delta T$$
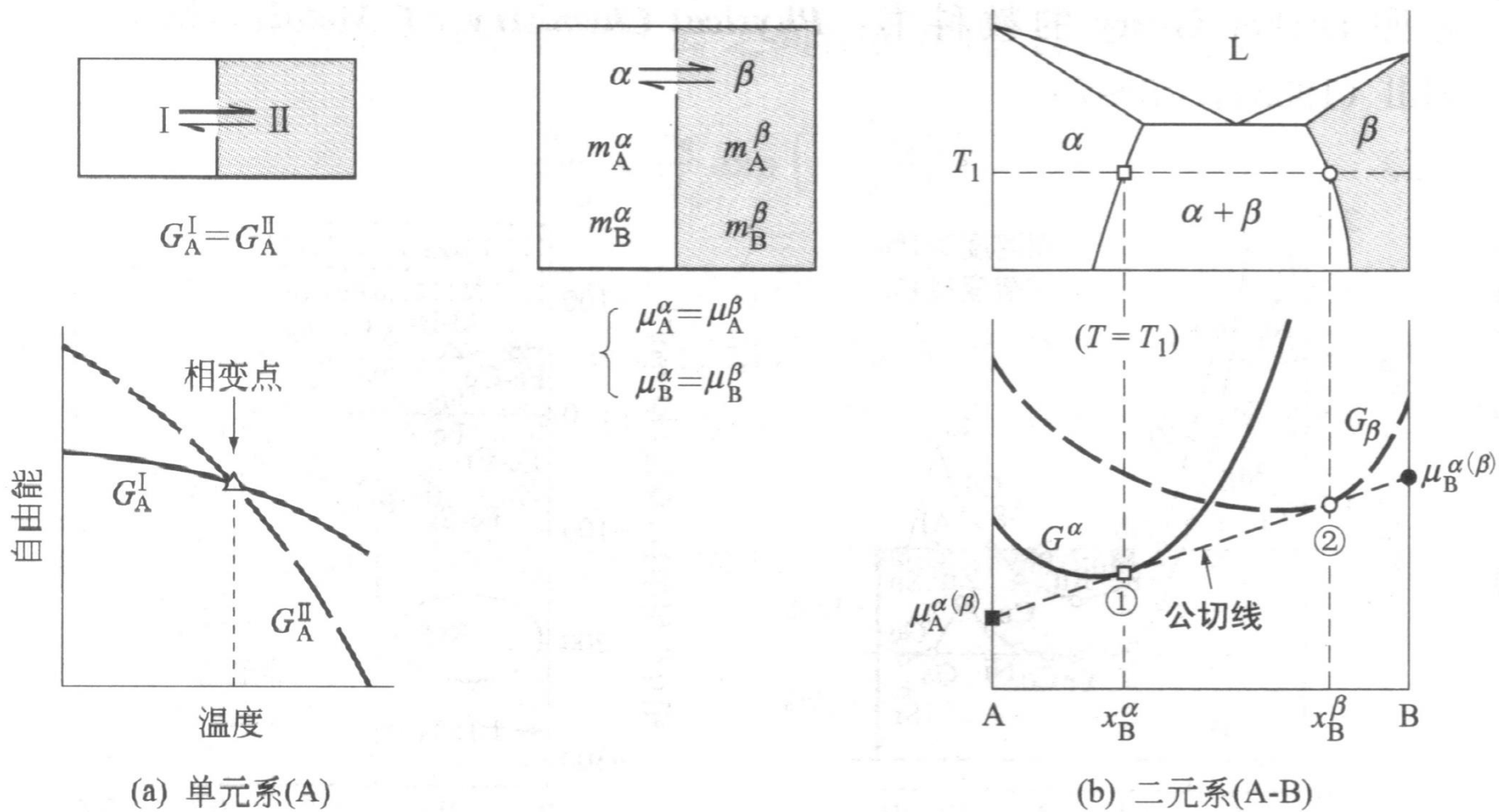
図 4.1 单元系和二元系的两相平衡条件

（a）单元系中自由能的交叉点是平衡温度；（b）二元系中公切线的切点
①和②是平衡成分

T. Nishizawa

Spinodal Points

Spinodal points
A special significance in the study of phase transformations

$$\left(\frac{\partial^2 \underline{G}_M}{\partial x_B^2}\right)_T = RT\left(\frac{1}{x_A} + \frac{1}{x_B}\right) - 2\varpi = 0$$

$$x_A x_B = \frac{RT}{2\varpi}$$

Figure 9.15 The miscibility gap, showing spinodal line.

Figure 9.13 Plots of properties of mixing versus composition for regular solutions: (a) molar enthalpy and (b) molar Gibbs free energy.

塑性加工过程中能量的分配（1/3）

将纯铁片进行强烈塑性加工所需的能量（约8 kJ·mol^{-1}）的大部分以热能形式消耗掉，其余的5%（**400 J·mol^{-1}**）左右以晶格缺陷的形式储存在试样中。

存储能量的大体比例为：

    1）约75%为位错增殖能；

    2）约10%为过剩空位能；

    3）其余的15%是应变能。

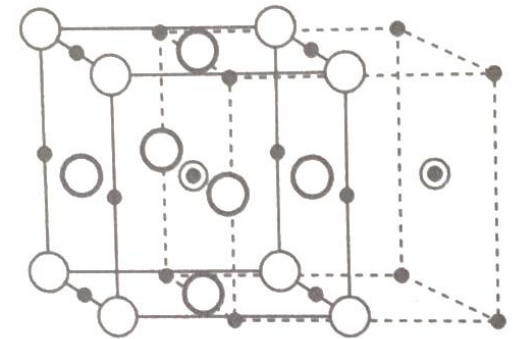如果假设位错能量为

空位形成能是
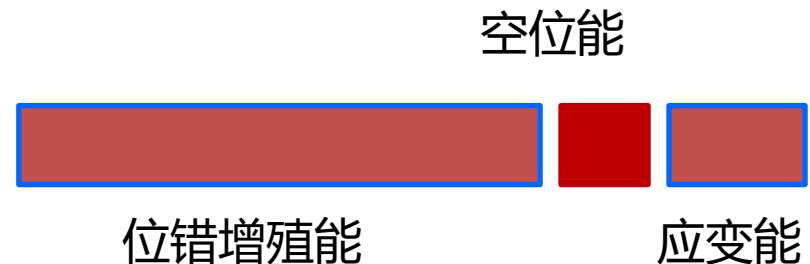
计算：由于强塑性加工所产生的位错密度和空位浓度？

空位能

位错增殖能　　　　应变能

$$\Delta e_d = 5 \times 10^{-9} \text{ J·m}^{-1}$$

$$\Delta e_v = 1.5 \text{ ev}$$

二元固溶体的亚点阵模型

- 模型的提出
- 熵与自由能

(a) γFe-C的晶格结构

- 溶体看成是有多个亚点阵组成，**固溶体的混合熵等于各亚点阵的混合熵之和**；

- **各亚点阵之间的相互作用可以忽略不计**；

- **超额Gibbs自由能描述同一亚点阵内组元的相互作用，此相互作用与其它亚点阵内组元的种类无关。**
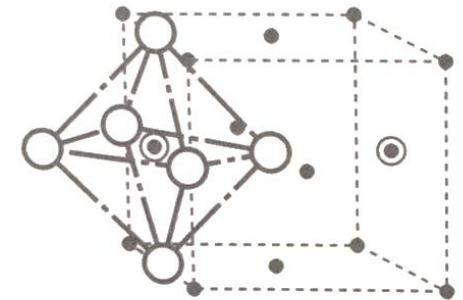
(b) C原子的间隙位置

亚点阵模型

表达成**通式**：

$$\sum^{M} x_i = \frac{a}{a+c} \qquad\qquad \sum^{N} x_i = \frac{c}{a+c} \qquad\qquad \frac{\sum^{M} x_i}{\sum^{N} x_i} = \frac{a}{c}$$

$$(M)_a(N)_c$$

在铁基合金bcc结构的亚点阵中，定义一个**新的参数**，即

$$y_{Fe} = \frac{x_{Fe}}{x_{Fe} + x_{Cr} + x_{Mn}} = \frac{x_{Fe}}{1/4} \qquad\qquad y_C = \frac{x_C}{x_C + x_N + x_v} = \frac{x_C}{3/4}$$
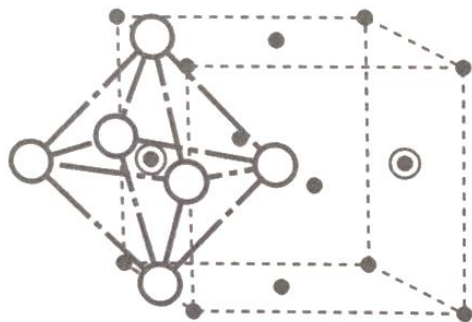
表达成通式，

$$y_{M_i} = \frac{x_{M_i}}{\frac{a}{a+c}} \qquad\qquad y_{N_i} = \frac{x_{N_i}}{\frac{c}{a+c}}$$

同一亚点阵上元素的摩尔分数之和为1.

fcc结构奥氏体晶体中可间隙溶入<15at%的碳(估算)
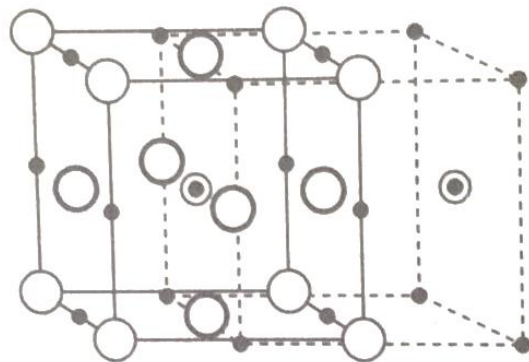
(a) γFe-C的晶格结构

(b) C原子的间隙位置

(c) 自由能曲线(1273 K)
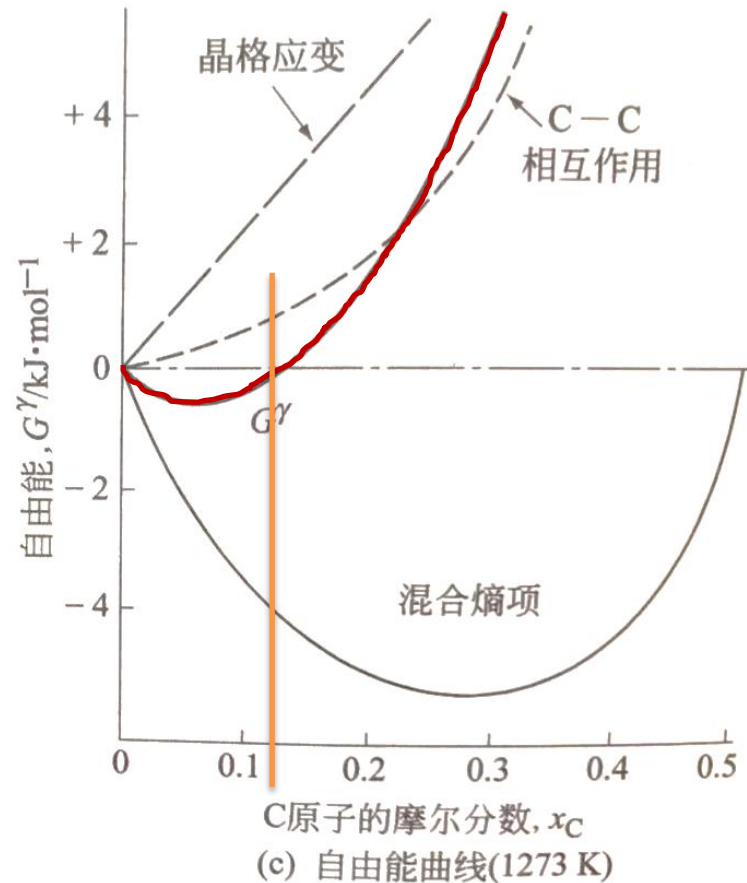
图 3.12 γFe-C 间隙式固溶体（奥氏体）的晶体结构和自由能
（C 原子的间隙位置处于 Fe 原子的八面体空隙的中心，所以称为八面体晶格间隙位置）

γFe-C系固溶体（奥氏体）中碳原子C的活度系数(1273 K)

$$\mu_C^\gamma = G^\gamma - (\frac{\partial G^\gamma}{\partial x_C})x_C + (\frac{\partial G^\gamma}{\partial x_C})$$

$$= \Delta G_C^\gamma - 2\,L_{C_v}^{\gamma Fe}\frac{x_C}{1-x_C} + RT[\ln x_C + ln(1-2x_C)]$$

$$\approx \Delta G_C^\gamma - 2\,(L_{C_v}^{\gamma Fe} - RT)x_C + RT\ln x_C$$

$$\mu_C^\gamma = RT\,ln a_C$$

$$\gamma_C = \frac{a_C}{x_C} \approx \exp(\frac{\Delta G_C^\gamma}{RT}) \cdot \exp[-2\left(\frac{L_{C_v}^{\gamma Fe}}{RT} - 1\right)x_C]$$
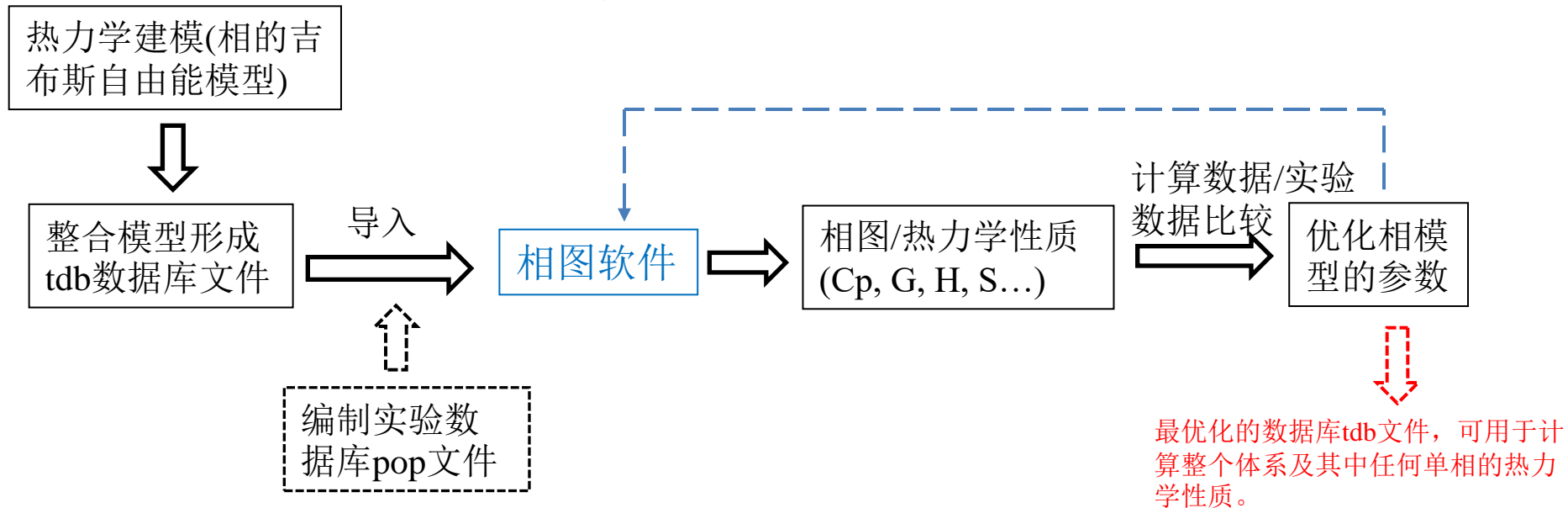
[稀溶体中的活度系数]　　　　[碳原子C之间的排斥作用]

1273K时，8.0*1.55 ~ **12. 活度极高，像是含有了 12倍浓度的碳原子**

CALPHAD相图计算方法：

基本流程

◆ tdb文件是CALPHAD统一的热力学数据库，所有的相图计算软件均遵守这种数据库格式。tdb文件包含对体系的组元的生成吉布斯自由能定义，以及体系中各稳定相的吉布斯自由能定义。

◆ pop文件是一种统一的实验数据库，用于某些相图软件中自动读取实验数据，实现自动优化参数的功能。pop文件包括：不变平衡方程的定义、相稳定温度定义、生成焓定义、熵定义、活度定义…

- 相变热力学
  - 新相的形成
  - **有序转变分析**
  - 凝固热力学
  - **脱溶分解**
  - Spinodal分解
  - **二级相变**热力学
  - 马氏体相变热力学

- 形状记忆合金与弹热效应

相变热力学

相变热力学的基本内容为计算相变驱动力，以相变驱动力大小决定相变的倾向，有时还能判定相变机制，在能够估算临界相变驱动力（在临界温度时所需的相变驱动力）的条件下，还可求得相变的临界温度。

相变：在均匀单相内，或在几个混合相中，出现不同成分或不同结构（包括原子、离子或电子位置及位向的改变）、不同组织形态或不同性质的相。(徐)

B-W-G模型对CuZn型有序化的分析

- 亚点阵与有序度
- 有序化引起的焓和熵的变化
- 平衡有序度

B-W-G模型 长程有序化模型

W. L. Braggs-E. J. Williams, 1934

W. S. Gorsky, 1928
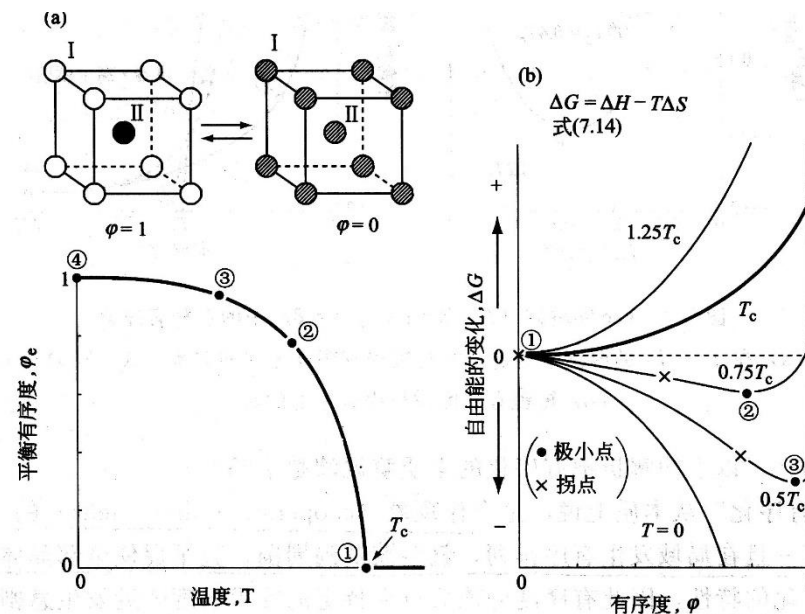
B-W-G模型对CuZn型(BCC)有序化的分析

亚点阵与有序度

$$\varphi = \frac{B_{II} - (B_{II})_0}{(B_{II})_1 - (B_{II})_0}$$

$$A_I + B_I = A_{II} + B_{II} = N/2$$

$$(B_{II})_1 = N/2 \qquad (B_{II})_0 = N/4$$

$$A_I = B_{II} = \frac{N}{4}(1 + \varphi)$$
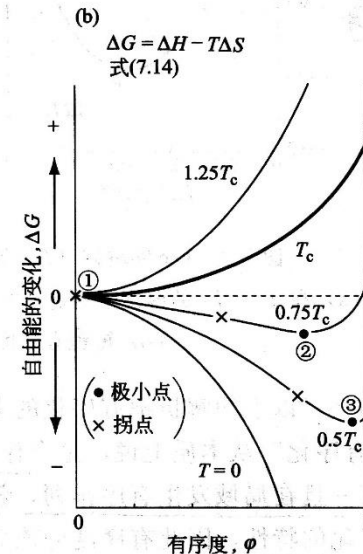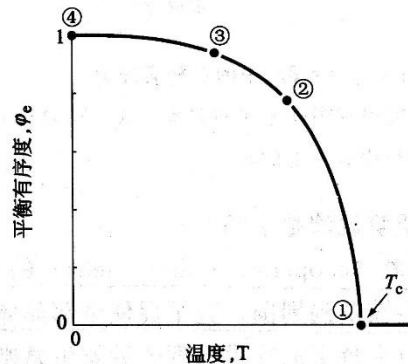
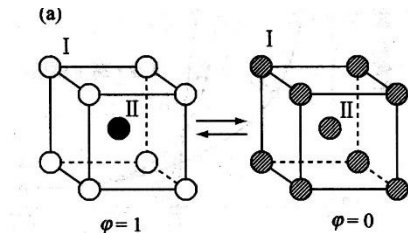$$A_{II} = B_I = \frac{N}{4}(1 - \varphi)$$

B-W-G模型对CuZn型有序化的分析

平衡有序度

$$(\Delta G)_{有序化} = (\Delta H)_{有序化} - T(\Delta S)_{有序化}$$

$$= \frac{\Omega_{AB}}{4}\varphi^2 + \frac{RT}{2}\left[(1+\varphi)\ln(1+\varphi) + (1-\varphi)\ln(1-\varphi)\right]$$

$$\left[\frac{(\Delta G)_{有序化}}{\partial \varphi}\right]_{\varphi=\varphi_e} = \frac{\Omega_{AB}}{2}\varphi_e + \frac{RT}{2}\ln\left(\frac{1+\varphi_e}{1-\varphi_e}\right) = 0$$

$$T_C = -\frac{\Omega_{AB}}{2R}$$

B-W-G模型对CuZn型有序化的分析

B-W-G模型对A:B≠1:1固溶体随着CuZn型有序化分析：Tc和热容

$$(\Delta H)_{有序化} = \Omega_{AB} x_B{}^2 \varphi^2$$

$$(\Delta S)_{有序化} =$$

$$-\frac{R}{2}\{[1 - x_B(1-\varphi)]\ln[1 - x_B(1-\varphi)]$$

$$+[x_B(1-\varphi)]\ln[x_B(1-\varphi)]$$

$$+[1 - x_B(1+\varphi)]\ln[1 - x_B(1+\varphi)]$$

$$+[x_B(1+\varphi)]\ln[x_B(1+\varphi)]$$

$$-2[(1-x_B)\ln(1-x_B) + x_B \ln x_B]\}$$

Minimum

$$-\frac{4\Omega_{AB}}{RT} x_B \varphi_e = \ln\{(\frac{1+\varphi_e}{1-\varphi_e})[\frac{1 - x_B(1-\varphi_e)}{1 - x_B(1+\varphi_e)}]\}$$

脱溶（沉淀）分解

固溶体α在一定温度下脱溶析出β固溶体

$$\Delta G = n_1(G_1 - G) + n_2(G_2 - G)$$

质量平衡 $\quad n_1(x - x_1) = n_2(x_2 - x)$

$$\Delta G = n_2 \left\{ (G_2 - G) + \left[\frac{(G_1 - G)(x_2 - x)}{x - x_1} \right] \right\}$$

$$n_1 \gg n_2$$

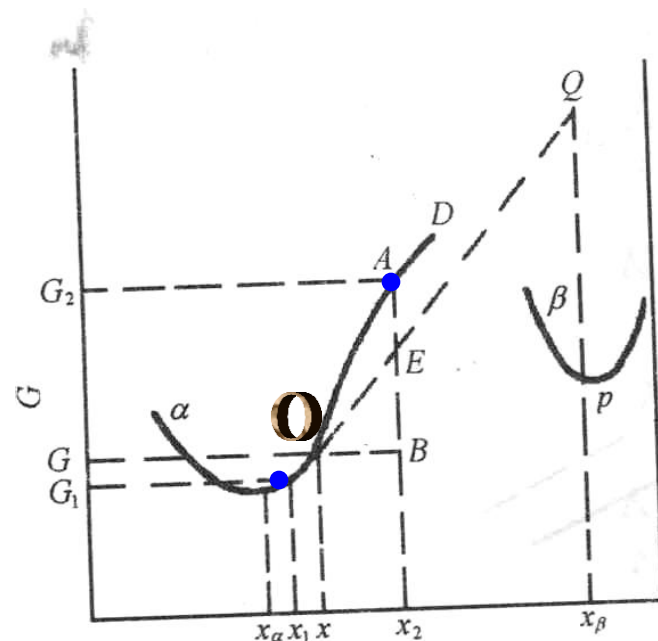$$\Delta G = n_2 \left\{ (G_2 - G) - (x_2 - x)\left(\frac{dG}{dx}\right)_x \right\}$$

图 12-12 α 固溶体脱溶分解为 β 相时的自由能变化

表面能

Surface energy based on Gibbs free energy

$$dG = -SdT + VdP + \gamma dA$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P}$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P} = \left(\frac{\partial U}{\partial A}\right)_{S,V} = \left(\frac{\partial H}{\partial A}\right)_{S,P} = \left(\frac{\partial F}{\partial A}\right)_{T,V}$$

Commonly observed manifestations

A liquid droplet tries to minimize its free energy, it assumes a spherical shape
Small droplets tend to agglomerate into larger droplets, minimizing their combined surface-to-volume ratios
Small particles of metals or ceramics, when pressed into a shape and heated at high temperatures, will "sinter" into a solid mass.

If we cleave a face-centered cubic crystal along a (111) plane, three bonds per atom will be broken. Two surfaces formed, the work required to form the surfaces will be 3ε/2 per surface atom.

$$w = \frac{3}{2}\varepsilon = \frac{\Delta H_S}{4N_A} \quad (for\ Z = 12)$$

$$\gamma = \frac{\Delta H_S}{4N_A}\left(\frac{N}{A}\right)$$

N/A is the number of atoms per unit area. For fcc structure:
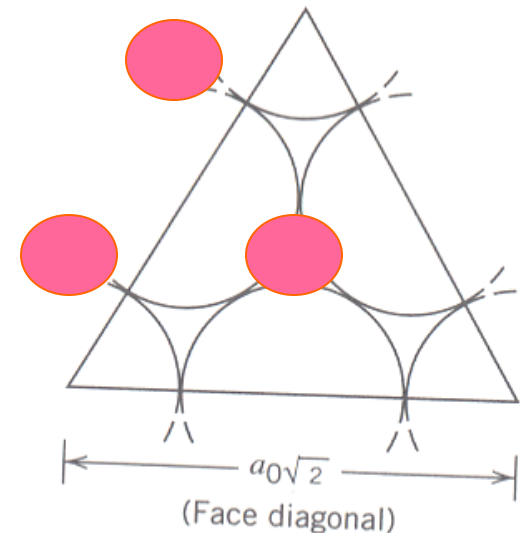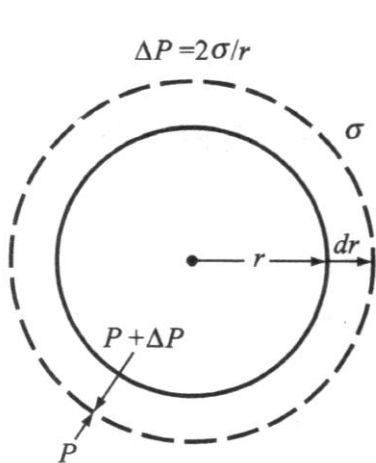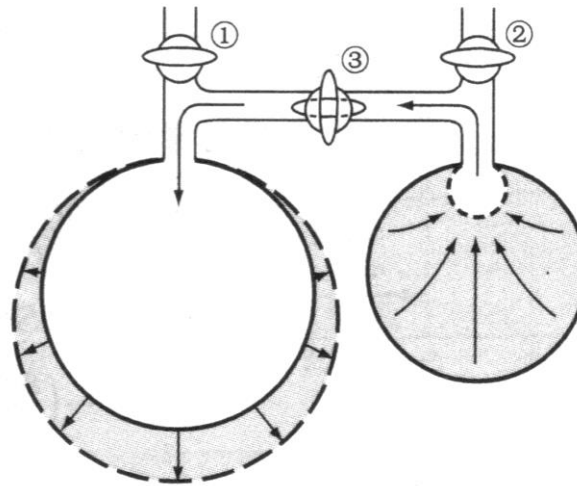
$$\frac{N}{A} = \frac{4}{\sqrt{3}a_0^2}$$

$a_0\sqrt{2}$
(Face diagonal)

Figure 4.2 Atomic packing on the (111) face of a face-centered cubic crystal.

Gibbs-Thomson效应 之 肥皂泡实验

(a) 由表面张力造成的内压

(b) 两个肥皂泡的实验

图 5.4 （a）拉普拉斯公式的图解；（b）小肥皂泡收缩而大肥皂泡膨胀

$$\Delta P = \frac{2\sigma}{r}$$

半径增加dr时
伴随表面积增加所增加的能量
伴随体积增加所消耗的能量

$$\sigma \cdot d(4\pi r^2) = \sigma \cdot 8\pi r dr$$

$$\Delta P \cdot d(4\pi r^3 / 3) = \Delta P \cdot 4\pi r^2 dr$$

From T. Nishizawa

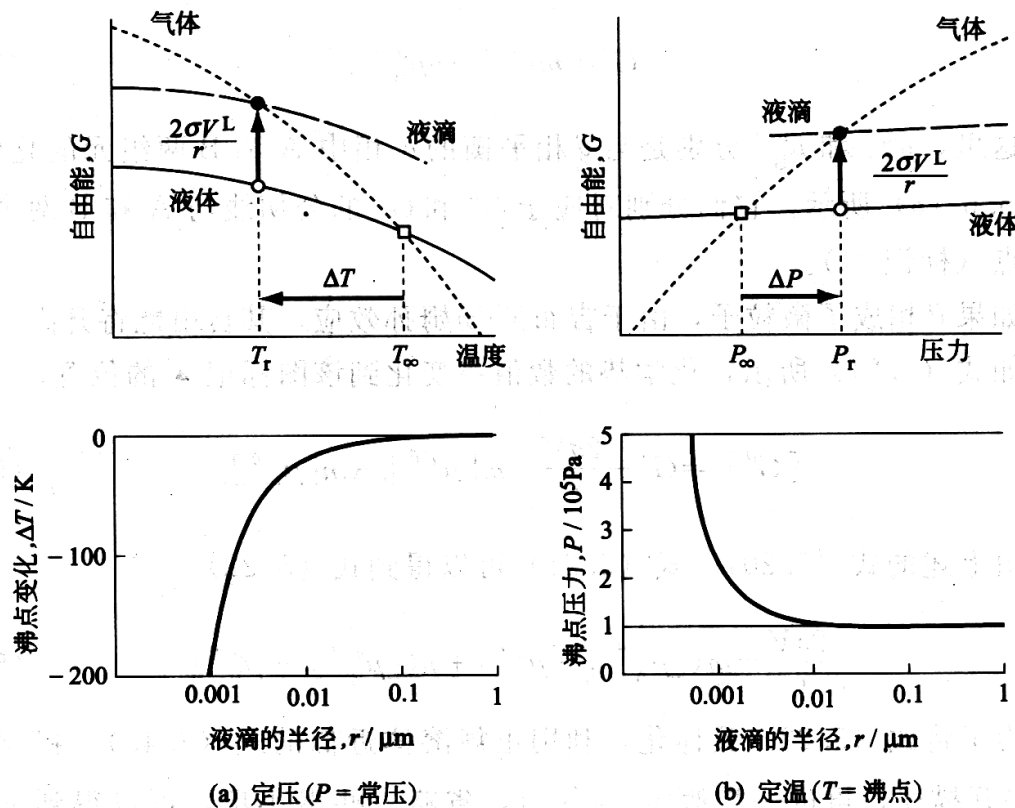图 5.5 由微粒化带来的沸腾温度下降和沸腾压力上升

由表面（界面）张力所引起的相平衡的变化，一般被称作 GibbsThomson效应

[**例题 5.6**] 试证明，分散在 α 相中的 θ 相（AmBn）的溶解度，会随 θ 相粒子的变小而以式（5.19）的形式增大。

$$[x_B^\alpha]_r \approx x_B^{\alpha/\theta} \cdot \exp\left[\frac{1}{nRT}\left(\frac{2\sigma V}{r}\right)\right] \qquad (5.19)$$

这里，σ 是 α/θ 界面的能量，V 是 θ 相的摩尔体积，$x_B^{\alpha/\theta}$ 是平衡溶解度（摩尔分数）。
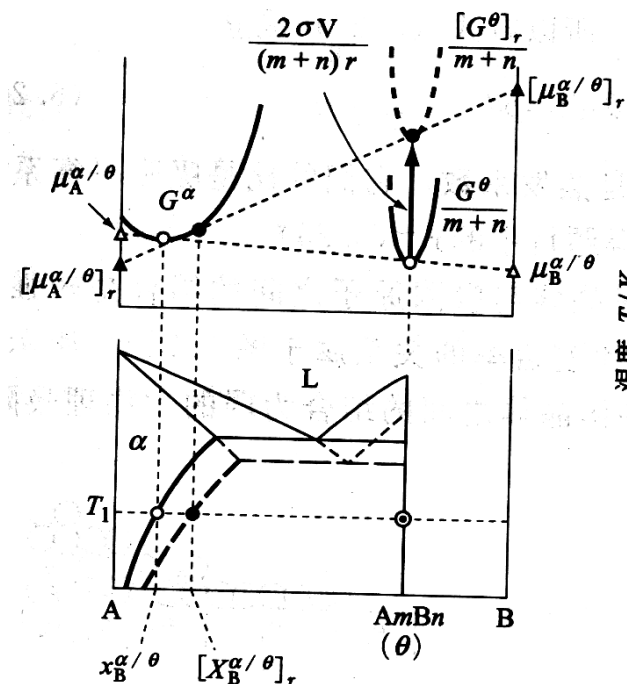
(a) 自由能图与相图
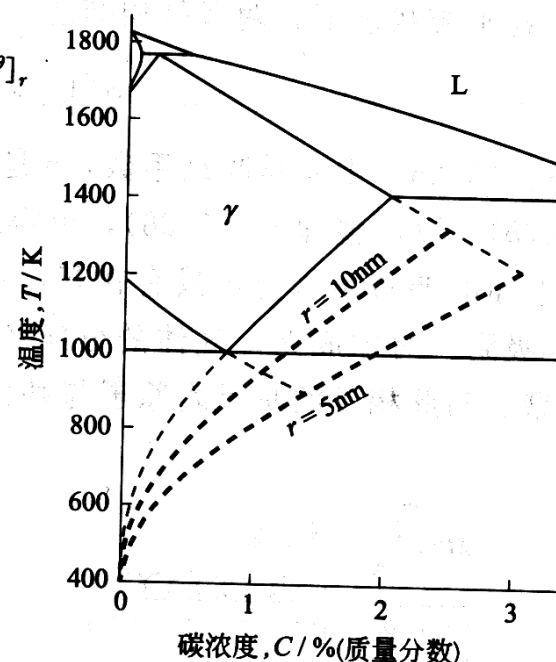
(b) Fe₃C在Fe-C系奥氏体中的溶解度曲线

图 5.6 由微粒化带来的溶解度增加

McLean(麦克林)晶界偏析公式

$$X^{gb} \approx \frac{x^\alpha \cdot \exp(\frac{\Delta\varepsilon_X^{gb}}{k_B T})}{1 + x^\alpha \cdot \exp(\frac{\Delta\varepsilon_X^{gb}}{k_B T})}$$

构成晶界的原子总数N^{gb}，偏析在晶界处的溶质原子的数目n^{gb}

晶粒内部的原子总数N^α，其中溶质原子的数目为n^α

1个溶质原子的晶界偏析能 $\Delta\varepsilon_X^{gb}$ 溶质原子的分布服从Maxell-Boltzman分布

$$\Delta G \approx -\Delta\varepsilon_X^{gb} \cdot n^{gb} - T \cdot k_B \cdot \ln[\frac{N^{gb}!}{n^{gb}!(N^{gb}!-n^{gb}!)} \cdot \frac{N^\alpha!}{n^\alpha!(N^\alpha!-n^\alpha!)}]$$

$$\ln[] \approx -[n^{gb}\ln(\frac{n^{gb}}{N^{gb}}) + (N^{gb}-n^{gb})\ln(\frac{N^{gb}-n^{gb}}{N^{gb}}) + n^\alpha\ln(\frac{n^\alpha}{N^\alpha}) + (N^\alpha-n^\alpha)\ln(\frac{N^\alpha-n^\alpha}{N^\alpha})]$$

$$0 = \frac{\partial \Delta G}{\partial n^{gb}} - \frac{\partial \Delta G}{\partial n^\alpha}$$

$$\approx -\Delta\varepsilon_X^{gb} + k_B T[\ln(\frac{n^{gb}}{N^{gb}}) - \ln(\frac{N^{gb}-n^{gb}}{N^{gb}}) - \ln(\frac{n^\alpha}{N^\alpha}) + \ln(\frac{N^\alpha-n^\alpha}{N^\alpha})]$$

$$= -\Delta\varepsilon_X^{gb} + k_B T \cdot \ln[\frac{(\frac{n^{gb}}{N^{gb}-n^{gb}})}{(\frac{n^\alpha}{N^\alpha-n^\alpha})}]$$

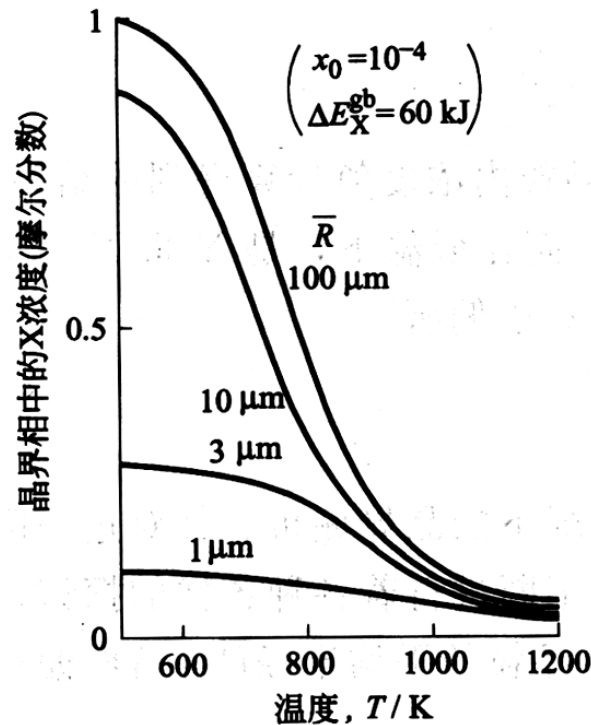$$\boxed{\frac{X^{gb}}{1-X^{gb}} \approx \frac{x^\alpha}{1-x^\alpha} \cdot \exp(\frac{\Delta\varepsilon_X^{gb}}{k_B T})}$$

晶粒超细化与晶界偏析的关系

晶内相自由能上升，平行切线变成公切线，直至非晶

(a)
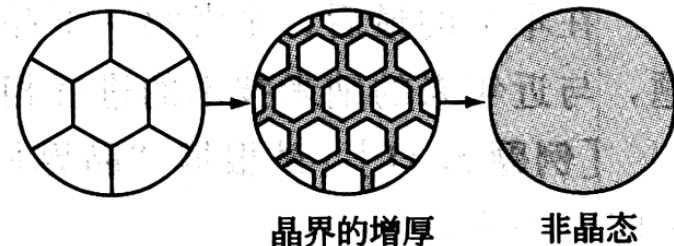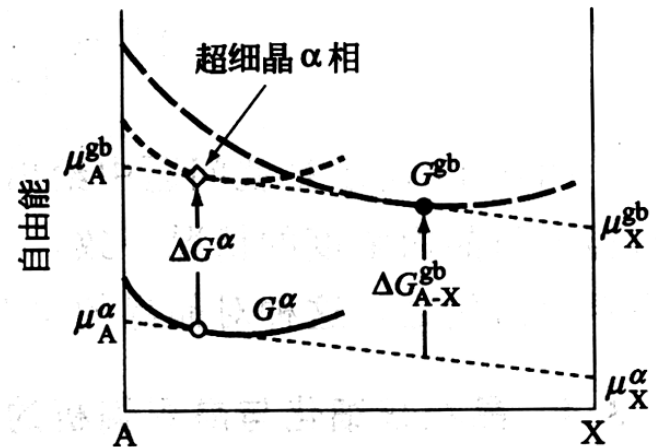
(b)

图 5.12 （a）由晶粒细化而带来的晶界偏析程度的减轻；

（b）由晶粒超细化带来的晶界增厚和非晶化

统计热力学

- 统计热力学

统计平均的方法研究大量微观粒子的力学行为，将统计力学应用于研
究热力学体系的宏观性质及其规律

统计热力学寻求的是在一定条件下对一切可能的微观运动状态的统计
平均值。

宏观世界　　　　　　统计热力学　　　　微观世界
（热力学）　　◄────────────►　　（量子力学）

Boltzman假定

- 熵和微观状态数之间的联系

混乱程度：熵、微观状态数

$$S = k \ln \Omega$$

k为Boltzmann常数

$$f(\omega) = f(\omega_A) + f(\omega_B)$$

$$\omega_{A,B} = \omega_A \cdot \omega_B$$

玻尔兹曼（*Ludwig Boltzmann*，1844-1906）奥地利理论物理学家，经典统计物理学的奠基人之一．在它的墓碑上寓意隽永地铭刻着

$$S = k \log W$$

Boltzmann Distribution

(a) 能级相等

(b) 能级不相等
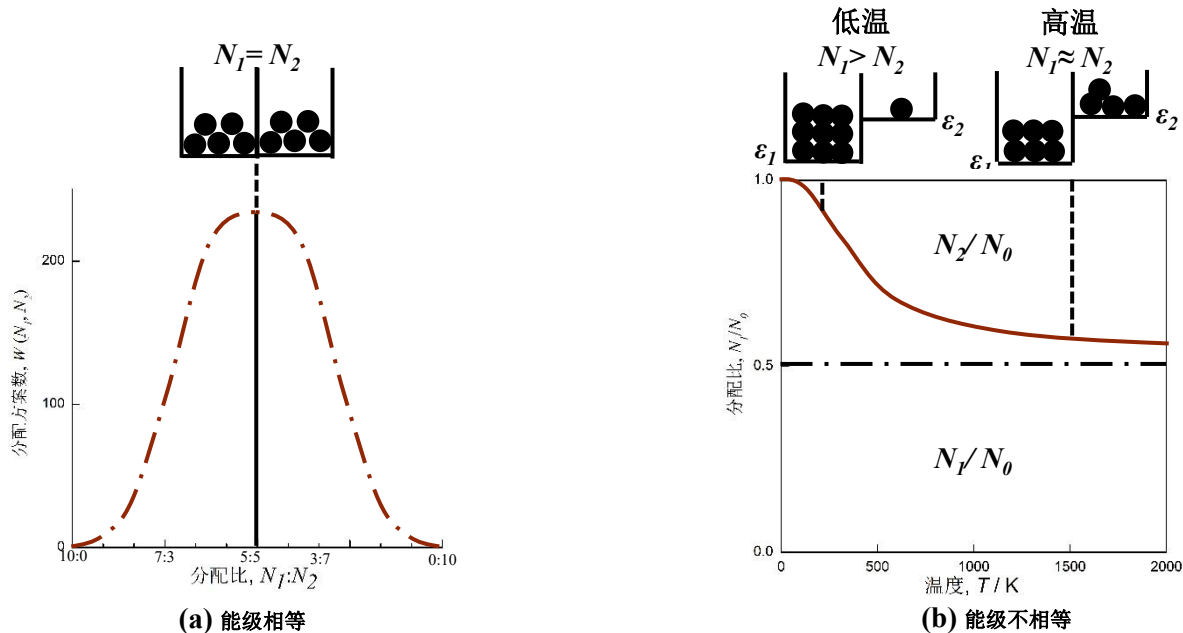
(a)能级相等时的均等分配；(b)能级不同时低温下倾向于分配在低能级，高温下近乎均等分配

$$\frac{N_1}{N_0} = \frac{exp\left(-\frac{\varepsilon_1}{k_B T}\right)}{exp\left(-\frac{\varepsilon_1}{k_B T}\right) + exp\left(-\frac{\varepsilon_2}{k_B T}\right)}$$

$$\frac{N_2}{N_0} = \frac{exp\left(-\frac{\varepsilon_2}{k_B T}\right)}{exp\left(-\frac{\varepsilon_1}{k_B T}\right) + exp\left(-\frac{\varepsilon_2}{k_B T}\right)}$$

Boltzmann Distribution

孤立体系/微正则系综 V、U、N

$$Maximize : \delta \ln \Omega = -\sum_{i=0} \left(\delta n_i \ln n_i \right) = 0$$

$$Constraint : \delta U = \sum_i \varepsilon_i \delta n_i = 0$$

$$Constraint : \delta N = \sum_i \delta n_i = 0$$

The Lagrange undetermined multipliers

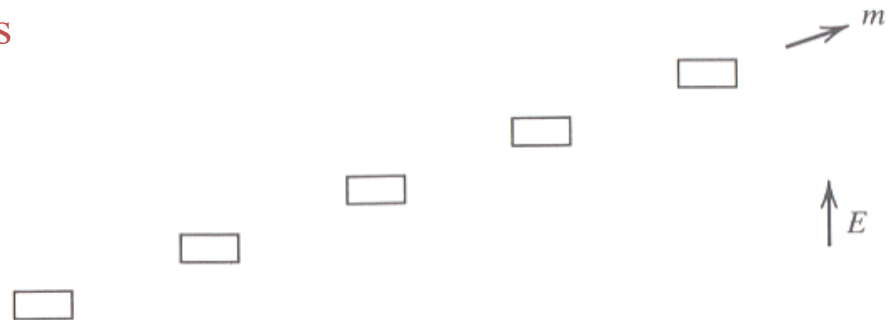|	Multiplier
$\sum_{i=0} \left(\delta n_i \ln n_i \right) = 0$	1
$\delta U = \sum_i \varepsilon_i \delta n_i = 0$	β
$\delta N = \sum_i \delta n_i = 0$	α

Figure 10.5 The m locations at different energy levels.

$$\boxed{\beta = \frac{1}{kT}}$$

$$U = \sum_i \varepsilon_i n_i = \sum \frac{N}{Z} \varepsilon_i e^{-\beta \varepsilon_i}$$

$$\sum \varepsilon_i e^{-\beta \varepsilon_i} = \frac{UZ}{N}$$

$$\boxed{Z \equiv \sum_i e^{-\beta E_i}}$$

$$S = k \ln \Omega = k(N \ln N - \sum n_i \ln n_i) = k(N \ln Z + \beta U)$$

$$\boxed{\left(\frac{\partial S}{\partial U}\right)_V = \frac{kN}{Z}\left(\frac{\partial Z}{\partial U}\right)_V + k\beta + kU(\frac{\partial \beta}{\partial U})_V = k\beta}$$

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

$$dU = TdS - pdV$$

$$\boxed{\left(\frac{\partial U}{\partial S}\right)_V = T}$$

$$\boxed{Z \equiv \sum_i e^{-E_i / kT}}$$

配分函数

体系中所有的热力学性质都可以由配分函数表达

单粒子体系 N＝1时

$$S = kN \ln Z + \frac{U}{T} = k \ln Z + \frac{U}{T}$$

$$U = \sum_i E_i P_i = \sum_i E_i \frac{\exp(-E_i/kT)}{Z} = \frac{1}{Z} \sum E_i \exp\left(-\frac{E_i}{kT}\right)$$

$$Z = \sum_i \exp\left(-\frac{E_i}{kT}\right)$$

$$\left(\frac{\partial Z}{\partial T}\right)_V = \sum_i \exp\left(-\frac{E_i}{kT}\right)\frac{E_i}{kT^2}$$

$$\left(\frac{\partial Z}{\partial T}\right)_V = \frac{1}{kT^2} \sum_i E_i \exp\left(-\frac{E_i}{kT}\right)$$

$$U = \frac{1}{Z} kT^2 \left(\frac{\partial Z}{\partial T}\right)_V = kT^2 \left[\frac{\partial(\ln Z)}{\partial T}\right]_V$$

$$S = k \ln Z + kT \left(\frac{\partial \ln Z}{\partial T}\right)_V$$

$$F = U - TS = -kT \ln Z$$

配分函数

能级的简并

粒子在能级中特定状态的几率

$$P_i = \frac{\exp(-\varepsilon_i/kT)}{Z}$$

特定能级

g_i 能级的简并度

$$P_i = \frac{g_i \exp(-\varepsilon_i/kT)}{Z}$$

$$Z = \sum g_i \exp(-\varepsilon_i/kT)$$

存在能级简并的粒子分布

统计热力学中的配分函数

平动配分函数

$$Z_t = \left(2\pi mkT / h^2\right)^{3/2} V$$

$$Z_t = \sum_{n_x}\sum_{n_y}\sum_{n_z} \exp\left[\frac{-(n_x^2 + n_y^2 + n_z^2)h^2}{8ma^2kT}\right] = \left\{\sum_n \exp\left[\frac{-n^2h^2}{8ma^2kT}\right]\right\}^3$$

理想气体的状态方程、性质

Ideal Gas

体积为V的立方盒中运动，三维平动

$$Z_{xyz} = Z_x Z_y Z_z = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} L^3 = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

$$\underline{F} = -N_A kT \left(\ln \frac{Z}{N_A} + 1 \right)$$

$$\boxed{P = \frac{N_A kT}{\underline{V}} = \frac{RT}{\underline{V}}}$$

$$P = -\left(\frac{\partial \underline{F}}{\partial \underline{V}} \right)_T \qquad P = \left(\frac{\partial \left[N_A kT \left(\ln \frac{Z}{N_A} + 1 \right) \right]}{\partial \underline{V}} \right)_T = N_A kT \left(\frac{\partial \ln Z}{\partial \underline{V}} \right)_T$$

统计热力学中的配分函数：费米-狄拉克和波色-爱因斯坦分布

费米-狄拉克分布

$$C_{g_i}^{n_i} = \frac{g_i!}{n_i!(g_i - n_i)!}$$

$$\omega_F(\{n_i\}) = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \qquad \sum_i n_i = N$$

$$\sum_i n_i \varepsilon_i = E$$

$$F(\{n_i\}) = \ln \omega_F + \alpha(N - \sum_i n_i) + \beta(E - \sum_i n_i \varepsilon_i) = 0$$

$$\frac{\partial F}{\partial n_i} = 0 \qquad n_i = \frac{g_i}{[\exp(\alpha + \beta \varepsilon_i) + 1]} \qquad n_j = \frac{1}{[\exp(\alpha + \beta \varepsilon_j) + 1]}$$

统计热力学中的配分函数：费米-狄拉克和波色-爱因斯坦分布

波色-爱因斯坦分布

$$C_{g_i}^{n_i} = \frac{(n_i + g_i - 1)}{n_i!(g_i - n_i)!}$$

$$\omega_B(\{n_i\}) = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - n_i)!}$$

$$F(\{n_i\}) = \ln \omega_B + \alpha(N - \sum_i n_i) + \beta(E - \sum_i n_i \varepsilon_i) = 0$$

$$\frac{\partial F}{\partial n_i} = 0 \qquad n_i = \frac{g_i}{[\exp(\alpha + \beta \varepsilon_i) - 1]}$$

$$n_j = \frac{1}{[\exp(\alpha + \beta \varepsilon_j) - 1]}$$

统计热力学中的配分函数：费米-狄拉克和波色-爱因斯坦分布

三种分布的关系

$$\alpha = \ln(Z/N)$$

$$Z = \left[2\pi mkT / h^2\right]^{3/2} V$$

$$e^\alpha = Z/N = \left[2\pi mkT / h^2\right]^{3/2} V/N$$

$$\left[2\pi mkT / h^2\right]^{3/2} V/N \gg 1$$

$$\omega_F(\{n_i\}) = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} = \prod_i \frac{g_i(g_i-1)(g_i-2)\cdots(g_i-n_i+1)}{n_i!} \approx \prod_i \frac{g_i^{n_i}}{n_i!}$$

$$\omega_B(\{n_i\}) = \prod_i \frac{(n_i+g_i-1)!}{n_i!(g_i-n_i)!} = \prod_i \frac{(n_i+g_i)(n_i+g_i-1)(n_i+g_i-2)\cdots(n_i+g_i-n_i+1)}{n_i!} \approx \prod_i \frac{g_i^{n_i}}{n_i!}$$

局域熵产生率

热力学第二定律，

$$dS \geq \frac{\delta Q}{T}$$

等号用于可逆过程，不等号适用于不可逆过程

$$dS = d_e S + d_i S = \frac{\delta Q}{T} + d_i S \quad \Longleftarrow \quad \text{计算不可逆过程的熵产生！}$$

系统与外界交换热量而引起的熵变

可正可负，取决于系统是吸热还是放热

系统内部所发生的过程所引起的熵产生，不会取负值

如可逆，则熵产生为零，不可逆则大于零

热传导局域熵产生率

局域熵密度的产生率

$$\frac{d_i s}{dt} = J_q \cdot X_q$$

如果热传导遵从傅立叶定律

$$J_q = -k\nabla T$$

热传导系数，恒正

$$\frac{d_i s}{dt} = J_q \cdot \nabla \frac{1}{T} = -J_q \cdot \frac{\nabla T}{T^2} = k \frac{(\nabla T)^2}{T^2} > 0$$

温差电现象

两种不同金属相连接，并在接头处保持不同的温度，线路中同时存在温度梯度和化学势梯度，因而同时产生热流和粒子流（电流）

- 塞贝克效应

- 珀尔帖效应

- 汤姆孙效应

- 焦耳效应

- 热传导效应