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## **Review previous**

Macro-states and Micro-states

Boltzmann Hypothesis and the Third Law

Boltzmann Distribution

Partition Function

Ideal Gas

etc.



# 统计热力学Contents

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统计热力学概述

Boltzmann假定、分布和配分函数

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聚合物溶液的混合熵



# Nomenclature

Macroscopic thermodynamics

microscopic thermodynamics/statistical thermodynamics

Root-mean-square / average rate of motion

Macrosate / Microstate: 宏观态/微观态

The time average of the properties of a system is equivalent to the instantaneous average over the ensemble of the microstates available to the system.



## Nomenclature (2)

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Ensemble: 系综

Microcanonical / canonical / macrocanonical: 微/正则/巨

Degeneracy: 简并度

Partition function: 配分函数

David V. Ragone, Thermodynamics of Materials, John Wiley & Sons, Inc., 1995, Vol. I, Chap 10 & Vol. II, Chap 2..

江伯鸿, 材料热力学, 上海交通大学出版社, 1999, 第八章

徐祖耀, 李麟, 材料热力学, 科学出版社, 2000, 第九第十章



## • 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  
(热力学)



微观世界  
(量子力学)



# 统计热力学基础：经典与统计

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- 经典热力学

研究热现象基本规律的宏观理论，所研究对象是含有大量粒子的平衡体系，是以在经验或实验数据基础上总结出的三个定律为基础，利用反应热、热容、熵等热力学函数，研究平衡体系各宏观性质之间的相互关系，进而预示过程自动进行的方向和可能性。

- 统计热力学

研究热现象基本规律的微观理论，其研究对象仍是由大量微观粒子（包括分子、原子和离子等）所组成的体系。

！从体系内部粒子的微观运动性质及结构数据出发，以粒子普遍遵循的力学定律为基础，用统计的方法直接推求大量粒子运动的统计平均结果，以得到平衡体系各种宏观性质的具体数值。



# 统计热力学基础：经典与统计

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## 统计热力学：经典统计/量子统计

服从经典力学规律的微观粒子组成的体系称为经典粒子体系。

服从量子力学规律的微观粒子组成的体系称为量子粒子体系。

经典力学

“组合分析”理论和系综理论

同种粒子彼此可分辨

量子力学

Fermi-Dirac和Bose-Einstein以及系综理论

无法对全同粒子编号



# Average Velocity of Gas Molecules

Monatomic, ideal gas in equilibrium with its pressure and temperature

$$PV = nRT$$

某个性质的宏观平均值

- 1) 某个微观状态的性质
- 2) 系统可以处于的微观状态 (数)
- 3) 每个微观状态的几率 (系统在各个微观状态出现的几率)

$$C_V = \frac{3}{2} R$$





# 宏观态、微观态

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- 宏观态

体系的状态由几个状态参数如温度、体积和内能来描述。

An isolated system at equilibrium at a given volume.

- 微观态

需表征体系中所有粒子的状态，如所有分子的能量和速度。

Specify the position and velocity of all of the molecules in the system

The rate of motion of molecules in air at macroscopic equilibrium

$$\bar{v}^2 = 3kT / m = 23.4 \times 10^4 \quad m^2 / S^2$$

$$\bar{v} = 483 \quad m / S$$

In order to compute the macroscopic average of a property

- The property of each microstate
- Which microstates the system can be in
- The probability that the system will be in a given microstate

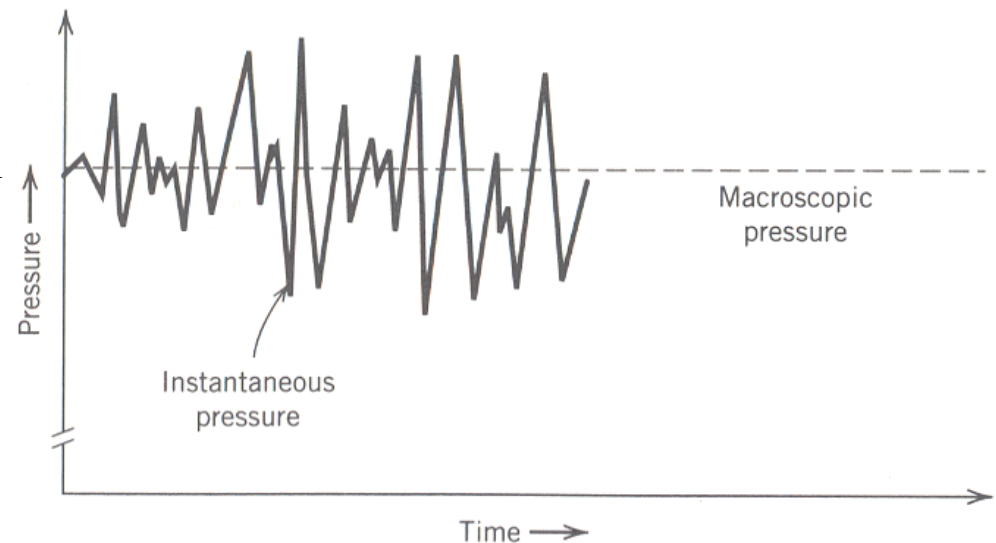
**Macrostate:**

stating the total number of particles in each box yields

**Microstate:**

each way of realizing a given macro distribution

Each macrostate may be realized by a number of microstates



**Figure 10.2** Instantaneous gas pressure as a function of time. (The magnitude of the variation of instantaneous gas pressure is exaggerated for emphasis.)



- 系综

微观态的总和，一个体系可以一系列微观态存在。

孤立体系 / 微正则系综

体积 $V$ 、粒子数 $N$ 和内能 $U$ 一定

封闭体系 / 正则系综

体积 $V$ 、粒子数 $N$ 和温度 $T$ 一定

敞开体系 / 巨正则系综

体积 $V$ 、温度 $T$ 一定， $\mu$



# 微观状态数与最可几分布

- 微观状态数

每一种分布即为一种微观态

微观态数目的多少表示体系内部混乱程度的大小

- 最可几分布

具有微观态数最多的分布出现的可能性最大

# 两个盒子中放置4个球

## Macrostate:

stating the total number of particles in each box yields

## Microstate:

each way of realizing a given macro distribution

Each macrostate may be realized by a number of microstates

**Table 10.1** Distributions of Four Spheres (A, B, C, and D) in Two Boxes I and II

	$\left[ \frac{ABCD}{0} \right]$	$\left[ \frac{BCD}{A} \right]$	$\left[ \frac{ACD}{B} \right]$	$\left[ \frac{ABD}{C} \right]$	$\left[ \frac{CD}{AD} \right]$	$\left[ \frac{BD}{AC} \right]$	$\left[ \frac{BC}{AD} \right]$	$\left[ \frac{A}{BCD} \right]$	$\left[ \frac{B}{ACD} \right]$	$\left[ \frac{C}{ABD} \right]$	$\left[ \frac{D}{ABC} \right]$	$\left[ \frac{0}{ABCD} \right]$
Box I	4	3	2	1								0
Box II	0	1	2	3								<del>4</del>
$\Omega$	1	4	6	4								1

微观状态数!



# 一种宏观态三个相同粒子的排列

量子力学

能量量子化（限定在一定体积内运动的粒子）

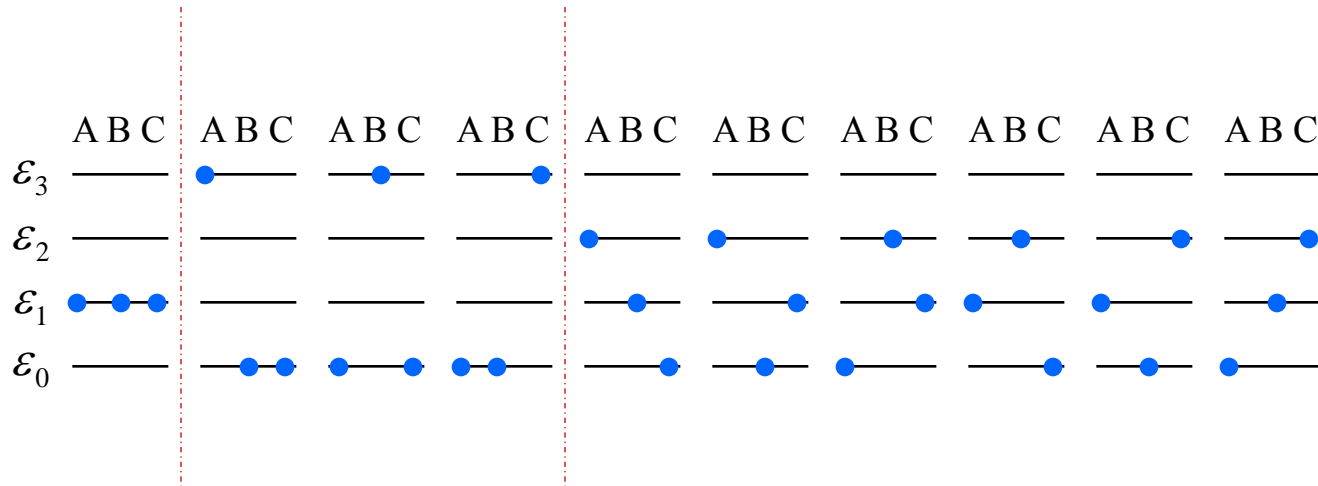
粒子运动的空间越小，能级之间的间距增加

$U=3u$ ,  $V$ (能级确定  $\varepsilon_0=0$ 、 $\varepsilon_1=1u$ 、 $\varepsilon_2=2u$ 、 $\varepsilon_3=3u$ ),  $N=3$



# 一种宏观态三个相同粒子的排列

$U=3u$ ,  $V$ (能级确定  $\varepsilon_0=0$ 、 $\varepsilon_1=1u$ 、 $\varepsilon_2=2u$ 、 $\varepsilon_3=3u$ ),  $N=3$



$$\omega_a = \frac{3!}{3!} = 1$$

$$\omega_b = \frac{3!}{2!1!} = 3$$

$$\omega_a = \frac{3!}{1!1!1!} = 6$$

$$\sum \omega = 10$$



# N个粒子的体系

U, V, N孤立体系/微正则系综 的一种分布态

能级:  $\varepsilon_0, \varepsilon_1, \varepsilon_2, \dots, \varepsilon_i, \dots, \varepsilon_r$

粒子数:  $n_0, n_1, n_2, \dots, n_i, \dots, n_r$

$$\sum_{i=0}^r n_i = N \quad \sum_{i=0}^r n_i \varepsilon_i = U$$

这种分布态的微观状态数目  $\omega$

$$\frac{N!}{\prod_{i=0}^r n_i!}$$

所有分布态微观状态数的总和称为体系的微观状态数  $\Omega$

$$\Omega = \sum_{i=0}^m \omega_i = \sum_{i=0}^m \frac{N!}{\prod_{i=0}^r n_i!}$$





# 微观态存在的机会和对 $\Omega$ 的贡献

- 平衡态？ / 稳态则常伴有能量流  
一个封闭系统经过足够长的时间自动达到所有宏观状态量都不再变化的状态。
- 基本假定
- 每个微观态等几率出现（ $U, V, N$ 确定的微正则系综）
- 最可几分布所代表的状态就是体系的平衡态（ $U, V$ 和 $N$ 确定）



# Boltzman假定

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- 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

微正则  
正则



# Isolated System and Boltzmann Hypothesis

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## Microcanonical ensemble

An isolated system with  $N$  particles in a volume,  $V$ , with a fixed energy,  $E$   
Premise: all microstates are equally probable

## Boltzmann hypothesis

The entropy of a system is linearly related to the logarithm of  $\Omega$

$$S = k \ln \Omega$$

$\Omega$ : thermodynamic probability

the number of different ways that macro-configuration can be achieved.

$$\Omega = \frac{N!}{N_I! N_{II}!}$$

Entropy of mixing of two components



## 统计热力学 熵的统计表达式

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

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

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

$$\omega_B f'(\omega_A \cdot \omega_B) = f'(\omega_A)$$

$$\omega_A \omega_B f''(\omega_A \cdot \omega_B) + f'(\omega_A \cdot \omega_B) = 0$$

$$\omega_{A,B} f''(\omega_{A,B}) + f'(\omega_{A,B}) = 0$$

$$\frac{df'(\omega_{A,B})}{f'(\omega_{A,B})} = \frac{d\omega_{A,B}}{\omega_{A,B}}$$

$$\ln f'(\omega_{A,B}) = \ln \frac{1}{\omega_{A,B}} + \ln k$$

$$f'(\omega_{A,B}) = \frac{k}{\omega_{A,B}}$$

$$f(\omega_{A,B}) = k \ln \omega_{A,B} + C$$

$$S = k \ln \omega_{A,B} + C$$

$$S = k \ln \omega$$

$$S = k \ln \Omega$$

$$\Omega = \frac{N!}{N_I! N_{II}!}$$

$$\underline{S}_M = k \ln \Omega = k \ln \frac{N_A!}{N_1! N_2!}$$

$$\underline{S}_M = k[\ln N_A! - \ln N_1! - \ln N_2!]$$

$$\underline{S}_M = k[N_A \ln N_A - N_A - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2]$$

$$\underline{S}_M = k[(N_1 + N_2) \ln N_A - N_1 \ln N_1 - N_2 \ln N_2]$$

$$\underline{S}_M = -k \left[ N_1 \ln \left( \frac{N_1}{N_A} \right) + N_2 \ln \left( \frac{N_2}{N_A} \right) \right]$$



# Isolated System and Boltzmann Hypothesis

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$$S = k \ln \Omega$$

$$\Omega = \frac{N!}{N_I! N_{II}!}$$

混合熵变

$$\underline{S}_M = -kN_A \left[ \frac{N_1}{N_A} \ln \left( \frac{N_1}{N_A} \right) + \frac{N_2}{N_A} \ln \left( \frac{N_2}{N_A} \right) \right]$$

$$\underline{S}_M = -R[x_1 \ln x_1 + x_2 \ln x_2]$$

$$\underline{S}_M = -R \sum_i x_i \ln x_i$$



# Boltzman分布

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- 求最可几分布的微观状态数

# Boltzmann Distribution

孤立体系/微正则系综  $V$ 、 $U$ 、 $N$

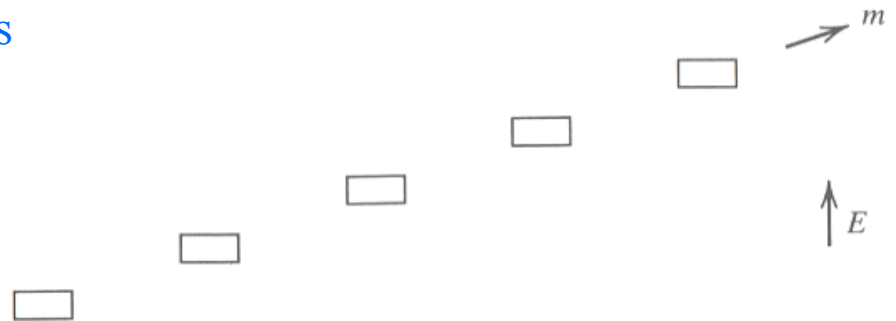
$$\text{Maximize: } \delta \ln \Omega = - \sum_{i=0} (\delta n_i \ln n_i) = 0$$

$$\text{Constraint: } \delta U = \sum_i \varepsilon_i \delta n_i = 0$$

$$\text{Constraint: } \delta N = \sum_i \delta n_i = 0$$

The Lagrange undetermined multipliers

	<u>Multiplier</u>
$\sum_{i=0} (\delta n_i \ln n_i) = 0$	1
$\delta U = \sum \varepsilon_i \delta n_i = 0$	$\beta$
$\delta N = \sum_i \delta n_i = 0$	$\alpha$



**Figure 10.5** The  $m$  locations at different energy levels.



$$\sum_i (\ln n_i + \alpha + \beta \varepsilon_i) \delta n_i = 0$$

$$\ln n_i + \alpha + \beta \varepsilon_i = 0$$

$$n_i = e^{-\alpha} e^{-\beta \varepsilon_i}$$

Z: Partition function

$$\sum n_i = N = e^{-\alpha} \sum_{i=0}^r e^{-\beta \varepsilon_i}$$

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

$$e^{-\alpha} = \frac{N}{Z}$$

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

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

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

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

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

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

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

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

$$dU = TdS - pdV$$

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

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



# 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

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

$g_i$  能级的简并度

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



# 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

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

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

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

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

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

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

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

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

# Distinguishability of Particles

$$\Phi = Z^N$$

$$\Phi = \frac{Z^N}{N!}$$

**Table 10.2** Partition Function for Many ( $N$ ) Noninteracting Particles ( $\Phi$ ) based on Partition Function for One Particle ( $Z$ )

Indistinguishable Particles (Gas)	Distinguishable Particles (Solid)
$\Phi = \frac{Z^N}{N!}$	$\Phi = Z^N$
$\ln \Phi = N \ln \frac{Z}{N} + N$	$\ln \Phi = N \ln Z$
$\left( \frac{\partial \ln \Phi}{\partial T} \right)_v = N \left( \frac{\partial (\ln Z)}{\partial T} \right)_v$	$\left( \frac{\partial \ln \Phi}{\partial T} \right)_v = N \left( \frac{\partial (\ln Z)}{\partial T} \right)_v$
$S = kN \left[ \ln \left( \frac{Z}{N} \right) + 1 \right] + NkT \left( \frac{\partial (\ln Z)}{\partial T} \right)_v$	$S = kN \ln Z + NkT \left( \frac{\partial (\ln Z)}{\partial T} \right)_v$
$F = -NkT \left( \ln \frac{Z}{N} + 1 \right)$	$F = -NkT \ln Z$
$P = - \left( \frac{\partial A}{\partial V} \right)_T = NkT \left( \frac{\partial (\ln Z)}{\partial V} \right)_T$	$P = - \left( \frac{\partial A}{\partial V} \right)_T = NkT \left( \frac{\partial (\ln Z)}{\partial V} \right)_T$



- 热力学的三个定律1? , 2?
- 理想气体的状态方程
- 熵、内能? 、热容的统计解释



# 熵的统计概念/第二定律

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影响微观状态数的因素就是影响熵的因素

- 熵的影响因素

- 聚集状态

- 温度

- 体积

- 分解反应

- 混合过程

表 8-2 一些物质在不同聚集状态下的标准熵  $S_m^\ominus / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

物 质	固 态	液 态	气 态
H <sub>2</sub> O	39.3	69.94	188.72
Pb	64.9	71.71	175.77
PbO	65.23	85.98	239.95
PbCl <sub>2</sub>	135.98	160.42	320.62



# 熵的统计概念/第二定律

- 热温熵



A:  $U_A, \Omega_A$

平衡条件:  $\delta \ln \Omega_A \Omega_B = 0$



B:  $U_B, \Omega_B$

$$\delta \ln \Omega_A = \frac{\delta q_A}{kT_A} \quad \delta \ln \Omega_B = \frac{\delta q_B}{kT_B} \quad -\delta q_A = \delta q_B = \delta q$$

$$\delta \ln \Omega_A \Omega_B = \delta \ln \Omega_A + \delta \ln \Omega_B = \left( \frac{1}{T_B} - \frac{1}{T_A} \right) \frac{\delta q}{k}$$





# 熵的统计概念/第二定律

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- 配置熵

N-n个A原子      n个B原子

混合前  $\Omega_1 = 1$

混合后  $\Omega_2 = ?$        $\Omega_2 = \frac{N!}{n!(N-n)!}$

$$\Delta_{mix} S_C = S_{C,2} - S_{C,1} = k \ln \Omega_2 - k \ln \Omega_1$$

Stirling近似       $x = \frac{n}{N}$

1 mol  $N_A$

$$\Delta_{mix} S_C = -Nk[x \ln x + (1-x) \ln(1-x)]$$

$$k = \frac{R}{N_A}$$



## • 振动熵

原子的振动视为谐振子

量子力学，频率为 $\nu$ 的一维谐振子的能量：

$$\varepsilon_i = (i + 1/2)h\nu, \quad i = 0, 1, 2, \dots$$

代入配分函数并展开为无穷级数

振动熵变？

高温

$$h\nu/kT \ll 1$$

$$Z \cong \frac{kT}{h\nu}$$

单个粒子

$$S = k \ln Z + kT \left( \frac{\partial \ln Z}{\partial T} \right)_V = k \left( \ln \frac{kT}{h\nu} + 1 \right)$$

每摩尔有 $3N_A$ 个振子

$$S_m = 3R \left( \ln \frac{kT}{h\nu} + 1 \right)$$



- 磁性熵

电子轨道磁距

每个离子，磁量子数 $m_l$ ,对固定的 $l$ 值，一共可取 $(2l+1)$ 个

无外磁场存在时， $N_A$ 个离子

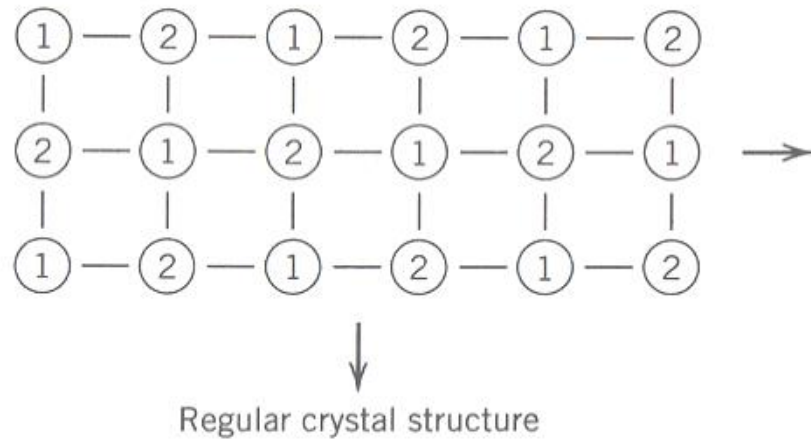
$$\Omega_{\text{磁性}} = (2l + 1)^{N_A}$$

$$S_{\text{磁性}} = N_A k \ln(2l + 1) = R \ln(2l + 1)$$

外场，电子自旋？

# Third Law

$$S = k \ln \Omega = 0$$



**Figure 10.3** Arrangement of atoms in a perfect compound.

# System at Constant Temperature

## Canonical ensemble

A closed system, with a fixed number of particles  $N$  and in a fixed volume  $V$ , immersed in a large constant temperature bath.

$$S = -k \sum_i P_i \ln P_i$$

$$P = \frac{1}{\Omega}$$

$$S = -k \sum_{i=1}^{i=\Omega} \frac{1}{\Omega} \ln \left( \frac{1}{\Omega} \right)$$

$$S = -k \Omega \left[ \frac{1}{\Omega} \ln \left( \frac{1}{\Omega} \right) \right]$$

$$S = k \ln \Omega$$

Gibbs formation identical to the Boltzmann formulation.

$P_i$

The probability that the system will be in microstate  $i$ , and the sum is the sum over all the microstate.



# Boltzmann Distribution

Find the distribution of  $N$  particles among the  $m$  energy levels that will maximize the entropy  $S$ , subject to the constraints.

$$\text{Maximize : } S = -k \sum_i P_i \ln P_i$$

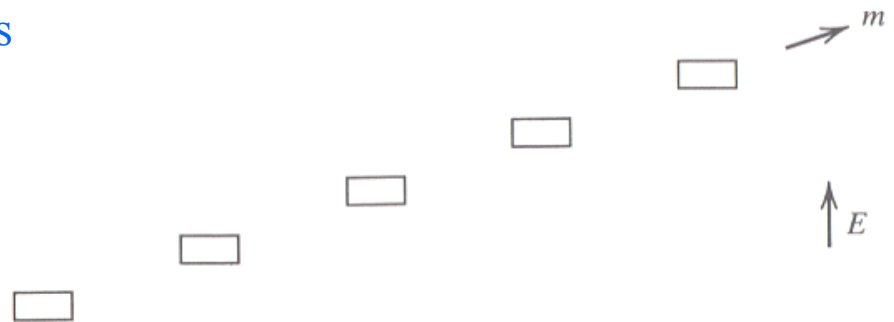
$$\text{Constraint : } \langle E \rangle = \sum_i P_i E_i$$

$$\text{Constraint : } 1 = \sum_i P_i$$

$\langle E \rangle$  The average energy or expected energy of a particle.

The Lagrange undetermined multipliers

	<u>Multiplier</u>
$\sum_i \ln P_i \delta P_i = 0$	1
$\sum_i E_i \delta P_i = 0$	$\beta$
$\sum_i \delta P_i = 0$	$-\ln \alpha$



**Figure 10.5** The  $m$  locations at different energy levels.

$$\sum_i (\ln P_i - \ln \alpha + \beta E_i) \delta P_i = 0$$

$$\ln P_i - \ln \alpha + \beta E_i = 0$$

$$P_i = \alpha e^{-\beta E_i}$$

$$\sum_i P_i = 1$$

$$\alpha \sum_i e^{-\beta E_i} = 1$$

$$\alpha = \sum_i e^{-\beta E_i}$$

$$P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$P_i = \frac{e^{-\beta E_i}}{Z}$$

Z: Partition function



$$S = -k \sum_i P_i \ln P_i = -k \sum_i P_i (-\ln Z - \beta E_i)$$

$$S = k \sum_i P_i \ln Z + k \sum_i \beta P_i E_i$$

$$S = k \ln Z + k \beta \langle E \rangle$$

$$S = k \ln Z + k \beta U$$

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

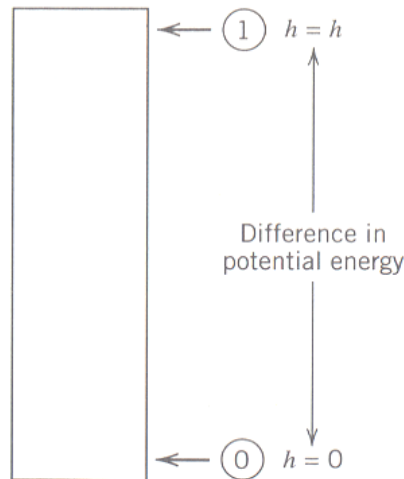


Figure 10.6 Isothermal column.

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

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

$$P_0 = \exp\left(\frac{-E_0}{kT}\right)$$

$$\frac{P_1}{P_0} = \exp\left(\frac{-E_1 - E_0}{kT}\right) = \exp\left(-\frac{mgh}{kT}\right)$$

$$\frac{\text{pressure}_1}{\text{pressure}_0} = \exp\left(-\frac{mgh}{kT}\right)$$

$$\text{pressure}_1 = \text{pressure}_0 \times \exp\left(-\frac{Mgh}{RT}\right)$$



# Partition Function

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

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

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

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

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

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

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

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



# 统计热力学中的配分函数：分子的运动状态与能级

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$$E = E_t + E_r + E_v$$

## 三维平动子的平动能

势阱边长

平动量子数

$$E_t = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

$$E_t = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$E_t = \frac{(p_x^2 + p_y^2 + p_z^2)}{2m}$$



# 统计热力学中的配分函数：分子的运动状态与能级

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## 刚性转子的转动能

$$E_r = \left( p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) / 2I$$

经典力学

量子力学

$$E_r = J(J+1)h^2 / (8\pi^2 I)$$

转动惯量



# 统计热力学中的配分函数：分子的运动状态与能级

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## 线性谐振子的振动能

$$E_v = p_r^2 / 2m + Kr^2 / 2$$

经典力学

$$E_v = (n + 1/2)h\nu$$

量子力学

$$E_v = (n_x + n_y + n_z + 3/2)h\nu$$

转动惯量



# 统计热力学中的配分函数：粒子的配分函数及其物理意义

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$$\mathcal{E} = \mathcal{E}_t + \mathcal{E}_r + \mathcal{E}_v + \mathcal{E}_e + \mathcal{E}_n + \cdots$$

$$Z = \sum_{j=1}^M e^{-\beta \mathcal{E}_j} = \sum_{t=1}^{M_t} \sum_{r=1}^{M_r} \sum_{v=1}^{M_v} \sum_{e=1}^{M_e} \sum_{n=1}^{M_n} e^{-\beta(\mathcal{E}_t + \mathcal{E}_r + \mathcal{E}_v + \mathcal{E}_e + \mathcal{E}_n + \cdots)}$$

$$Z = Z_t Z_r Z_v Z_e Z_n$$



# 统计热力学中的配分函数：粒子的配分函数及其物理意义

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## 平动配分函数

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

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



# 统计热力学中的配分函数：粒子的配分函数及其物理意义

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## 转动配分函数

$$Z_r = (8 / h^2) \pi^2 I k T$$

$$Z_r = \sum_{J=0}^{\infty} (2J+1) \exp \left[ -J(J+1) h^2 / (8 \pi^2 I k T) \right]$$

$$\Theta_r = h^2 / (8 \pi^2 I k T) \ll T$$

$$Z_r = \int_0^{\infty} (2J+1) \exp \left[ -J(J+1) \Theta_r / T \right] dJ = T / \Theta_r$$

$$Z_r = T / (\sigma \cdot \Theta_r)$$

$$Z_r = \left[ (\pi I_x I_y I_z)^{1/2} / \sigma \right] (8 \pi^2 k T / h^2)^{3/2} = (\pi^{1/2} / \sigma) (T^3 / \theta_x \theta_y \theta_z)^{1/2}$$

三个转动特征温度



# 统计热力学中的配分函数：粒子的配分函数及其物理意义

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## 振动配分函数

$$\nu = (k / m)^{1/2} / 2\pi$$

$$Z_v = kT / h\nu$$

$$Z_v = \sum_{n=0}^{\infty} \exp[-\beta(n + 1/2)h\nu] = \exp(-\Theta_v / 2T) / [1 - \exp(-\Theta_v / T)]$$

$$Z_v = T / \Theta_v = kT / h\nu$$

$$Z_v = 1 / [1 - \exp(-\Theta_v / T)]$$





# 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

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$$\omega(\{n_i\}) = \frac{N!}{\prod_i n_i!} \prod_i g_i^{n_i} = N! \prod_i \frac{g_i^{n_i}}{n_i!}$$

$$\omega(\{n_i\}) = \prod_i \frac{g_i^{n_i}}{n_i!}$$

$$n_i = g_i e^{-\alpha - \beta \varepsilon_i}$$

$$Z = \sum_{\lambda} g_i e^{-\beta \varepsilon_i}$$



# 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

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## 费米-狄拉克分布

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

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

$$\sum_i n_i \varepsilon_i = E$$

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

$$\frac{\partial F}{\partial n_i} = 0$$

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



# 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

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## 波色-爱因斯坦分布

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

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

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

$$\frac{\partial F}{\partial n_i} = 0$$

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

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



# 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

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## 三种分布的关系

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

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

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

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

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

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



# Ideal Gas

质量为 $m$ 的粒子在 $x$ 方向上长度为 $L$ 范围做一维平动

$$mv = \frac{h}{\lambda} \quad \lambda = \frac{2L}{i} \quad \text{运动速度} \quad v_x = \frac{h_L}{2mL} \bullet i$$

$$\text{能级能量} \quad E_x = \frac{1}{2}mv_x^2 = \frac{h^2 i^2}{8mL^2}$$

$$\text{X方向平动Z: } Z_x = \sum_{i=1}^{i=\infty} \exp\left(-\frac{E_i}{kT}\right) = \sum_{i=1}^{i=\infty} \exp\left[-\left(\frac{h^2}{8mL^2 kT}\right) i^2\right]$$

$$\text{求和改积分: } Z_x = \int_0^{\infty} \exp\left[\left(-\frac{h^2}{8mL^2 kT}\right) i^2\right] di$$

$$Z_x = \left(\frac{2\pi mkT}{h^2}\right)^{1/2} L$$

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2}$$



# Ideal Gas

体积为V的立方盒中运动，三维平动

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

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

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

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



# 晶体的热容

固体热容特点：

- 趋于0K时， $C_V$ 趋于0
- 较高温度， $C_V$ 约为3R/ Dulong-Petit定律
- 中间温度不符？

Einstein认为：晶体的热容来自依赖于温度的振动能量

单原子振动配分函数

$$Z = \frac{e^{u/2}}{e^u - 1} \quad u = \frac{\theta_E}{T} \quad \theta_E = \frac{h\nu}{k}$$

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

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = ku^2 \frac{e^u}{(e^u - 1)^2}$$

1mol晶体有3R个谐振子

$\theta_D$

Pb: 105 K

Cu: 343 K

金刚石: 2230 K

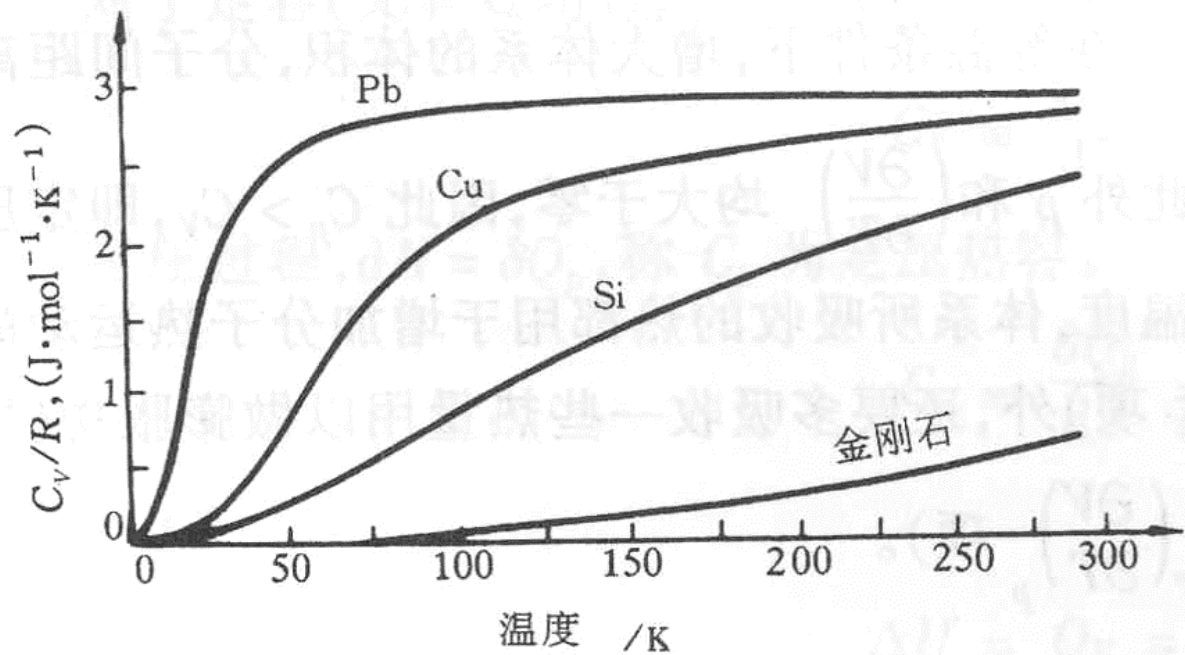


图 2-4 一些元素在不同温度下的摩尔热容量





# 晶体的热容

中间温度不符？

Debye认为：振动耦合  
频率分布函数：

$$\bar{C}_{V,m} = \frac{1}{3N_A} \sum_j g_j C_{V,mj}$$

连续变量的积分来近似：

$$\bar{C}_{V,m} = \frac{1}{3N_A} \int_0^{\nu_{\max}} g_j C_{V,mj} d\nu = 9R \left( \frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{u^4 e^u}{(e^u - 1)^2} du$$

$$\theta_D = \frac{h\nu_{\max}}{k}$$

较高温

较低温

$$\bar{C}_{V,m} = \frac{36}{15} \pi^4 R \left( \frac{T}{\theta_D} \right)^3$$



# 统计热力学基础：热容的理论表达式

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## 平衡条件的应用—热空位浓度的求解

$$\omega = \frac{(N+n)!}{N!n!}$$

$$\Delta S = k \ln[(N+n) \ln(N+n) - N \ln N - n \ln n] = -k \left[ N \ln \frac{N}{N+n} + n \ln \frac{n}{N+n} \right]$$

$$x_v = \frac{n}{N+n} = \exp\left(-\frac{\Delta u}{kT}\right)$$

$$\frac{n}{N} = \frac{1}{\exp(\Delta u/kT) - 1}$$



# 统计热力学基础：热容的理论表达式

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## 爱因斯坦方程

$$\frac{n}{3N} = \frac{1}{\exp(h\nu/kT) - 1}$$

$$\Delta U = n \cdot h\nu = \frac{3N}{\exp(h\nu/kT) - 1}$$

$$C_V = 3R \left( \frac{h\nu}{kT} \right)^2 \frac{\exp(h\nu/kT)}{[\exp(h\nu/kT) - 1]^2}$$

$$C_V = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T) - 1]^2}$$

$$C_V = 3R \left( \frac{\Theta_E}{T} \right)^2 \exp(-\Theta_E/T)$$

$$C_V = 234R \left( \frac{\Theta_E}{T} \right)^3$$



# 溶液的准化学键模型

非理想溶液的混合自由能与尺寸、电子结构和化学键等有关  
准化学键模型：只考虑最近邻原子间的相互作用/键能  
但对许多现象的理解很有价值

$n_A$  个A原子， $n_B$  个B原子， $n_A + n_B = N_0$

A-A键能： $u_{AA}$ ， $p_{AA}$ ；

B-B键能： $u_{BB}$ ， $p_{BB}$ ；

A-B键能： $u_{AB}$ ，均为负值， $p_{AB}$

原子配位数（最近邻原子数）： $z$



# 点阵统计理论和Ising模型

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微观的合金理论：

根据粒子间的相互作用，直接计算出自由能与温度和成分的关系

处理固溶体的统计理论模型和伊辛处理铁磁性问题的模型相似

A-B近邻对数为： $z p_{AB}$



# 亚点阵模型

Hillert, 2个亚点阵组成

$$(A, B)_a (C, D)_c$$

A,B表示处于一个亚点阵的两种元素  
a和c表示各亚点阵的位置数,  $a+c=1$

摩尔自由能

偏摩尔自由能

间隙溶液中的应用

亚点阵模型的扩展

铁基合金bcc结构

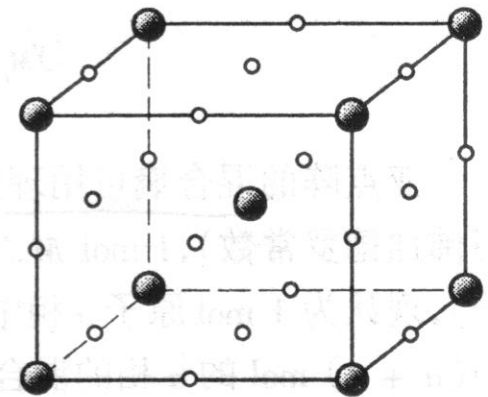
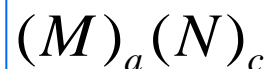
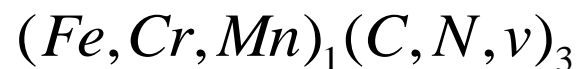
质点亚点阵：顶点和体心的质点 2个

间隙亚点阵：八面体间隙  $12 \times 1/4 + 6 \times 1/2 = 6$ 个

铁基合金

质点亚点阵：Fe、Cr、Mn等

间隙亚点阵：C、N、v(空位)等



● 质点位置 ○ 间隙位置

图 7.9 bcc 结构中八面体间隙位置示意图