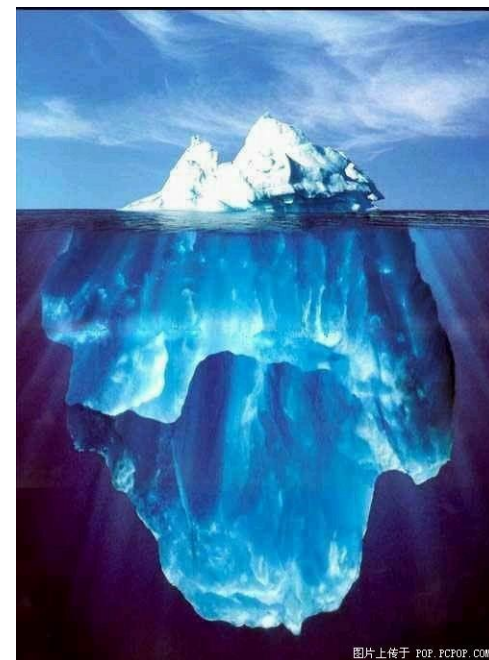


热学

Thermophysics

穆良柱



图片上传于 POP.FCPOP.COM

课程简介

- 课程名称：热学
- 学分：3
- 上课时间地点：周一3-4 ， 周四7-8(单周)， 理教402
- 成绩评定：平时10； 期中40； 期末50.
- 助教：叶柄天， 18811792232， yebingtian@126.com
韩兆宇， 15652626191， heinsius@pku.edu.cn
李泽阳， 13901221673， laser.li@pku.edu.cn
- 答疑时间和地点：预约， 理教111
- 联系方式：穆良柱， 13681016237， muliangzhu@pku.edu.cn

教材与参考书

- 教材讲义

- ppt讲义

- 刘玉鑫，《热学》，北京大学出版社，2016年4月；

- 习题，李椿《热学》，第二版，高等教育出版社，2008年。

- 参考书

- (1)赵凯华、罗蔚茵，新概念物理教程《热学》，高等教育出版社,1998；

- (2)包科达，《热物理学基础》，高等教育出版社，2002；

- (3)陆果，《基础物理学》下卷，高等教育出版社，1997；

- (4)林宗涵，《热力学与统计物理学》，北京大学出版社，2007。

课程目录

- [1 热学简介](#) 作业:
- [2 第零定律和温度](#) 作业: 1.8, 1.10
- [3 状态方程](#) 作业: 1.25, 1.32
- [4 物质微观图像](#) 作业: 7.1, 7.3
- [5 理想气体微观初级理论](#) 作业: 2.14, 2.20
- [6 麦克斯韦速度分布律](#) 作业: 3.19, 3.25
- [7 麦玻分布与能均分定理](#) 作业: 3.24, 3.30
- [8 基于量子力学的麦玻分布](#) 作业: 6.30
- [9 麦玻分布的检验与F-D分布、B-E分布](#) 作业:
- [10 气体分子的碰撞](#) 作业: 4.8, 4.12
- [11 气体的输运过程](#) 作业: 4.18, 4.21
- [12 热力学第一定律](#) 作业: 5.12, 5.16
- [13 热力学第一定律的应用](#) 作业: 5.24, 5.29
- [14 卡诺定理与热力学第二定律](#) 作业: 6.7, 6.8
- [15 克劳休斯不等式与熵](#) 作业: 6.27, 6.24
- [16 热力学第二定律的应用和讨论](#) 作业: 6.28, 6.29
- [17 热力学基本微分方程](#) 作业: 6.9, 6.10
- [18 热力学理论的应用](#) 作业: 6.13, 6.17
- [19 热辐射系统](#) 作业:
- [20 液体表面的热力学](#) 作业: 8.2, 8.5
- [21 相变现象及其热力学](#) 作业: 9.2, 9.13
- [22 范氏气体与气液相变](#) 作业: 9.8, 9.12

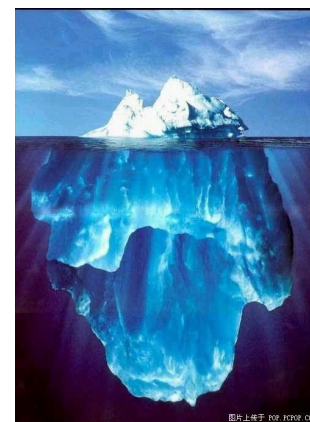
课程进度

周数	日期	星期	地点	上课时间	进度	教学内容	习题 (李椿《热学》)
1	2月20日	周一	理教402	10:10-12:00	01	什么是物理? 什么是热学?	
	2月23日	周四	理教402	15:10-17:00	02	温度与热力学第零定律	1.8, 1.10
2	2月27日	周一	理教402	10:10-12:00	03	理想气体的状态方程	1.25, 1.32
3	3月06日	周一	理教402	10:10-12:00	04	物质的微观图像	7.1, 7.3
	3月09日	周四	理教402	15:10-17:00	05	理想气体微观初级理论	2.14, 2.20
4	3月13日	周一	理教402	10:10-12:00	06	麦克斯韦速度分布律及其验证	3.19, 3.25
5	3月20日	周一	理教402	10:10-12:00	07	麦玻分布及其验证(能均分定理)	3.24, 3.30
	3月23日	周四	理教402	15:10-17:00	08	量子版本的麦玻分布及其验证	6.30
6	3月27日	周一	理教402	10:10-12:00	09	F-D统计与B-E统计及其应用	
7	4月03日	周一	理教402	10:10-12:00	10	气体分子碰撞的微观描述	4.8, 4.12
	4月06日	周四	理教402	15:10-17:00	11	输运过程	4.18, 4.21
	4月09日	周日	理教111	18:00-21:00		答疑	
8	4月10日	周一	理教402	10:10-12:00	12	期中考试	
9	4月17日	周一	理教402	10:10-12:00	13	热力学过程与热力学第一定律	5.12, 5.16
	4月20日	周四	理教402	15:10-17:00	14	第一定律的应用	5.24, 5.29
10	4月24日	周一	理教402	10:10-12:00	15	卡诺定理与热力学第二定律	6.7, 6.8
	4月25日	周二	理教303	18:40-20:30	16	克劳修斯不等式与热力学第二定律	6.27, 6.24
13	5月15日	周一	理教402	10:10-12:00	17	第二定律的应用与讨论(其他表述)	6.28, 6.29
	5月18日	周四	理教402	15:10-17:00	18	热力学基本微分方程(理想气体上)	6.9, 6.10
14	5月22日	周一	理教402	10:10-12:00	19	热力学理论的应用(范氏气体, 橡)	6.13, 6.17
15	5月29日	周一	理教402	10:10-12:00	20	相变现象及其热力学	9.2, 9.13
	6月01日	周四	理教402	15:10-17:00	21	范氏气体与气液相变, 连续相变理	9.8, 9.12
16	6月05日	周一	理教402	10:10-12:00	22	液体表面的热力学	8.2, 8.5
	6月11日	周日	理教111	18:00-21:00		答疑	
17	6月12日	周一	理教402	10:10-12:00	23	期末考试	

热学简介

热学研究对象—热现象

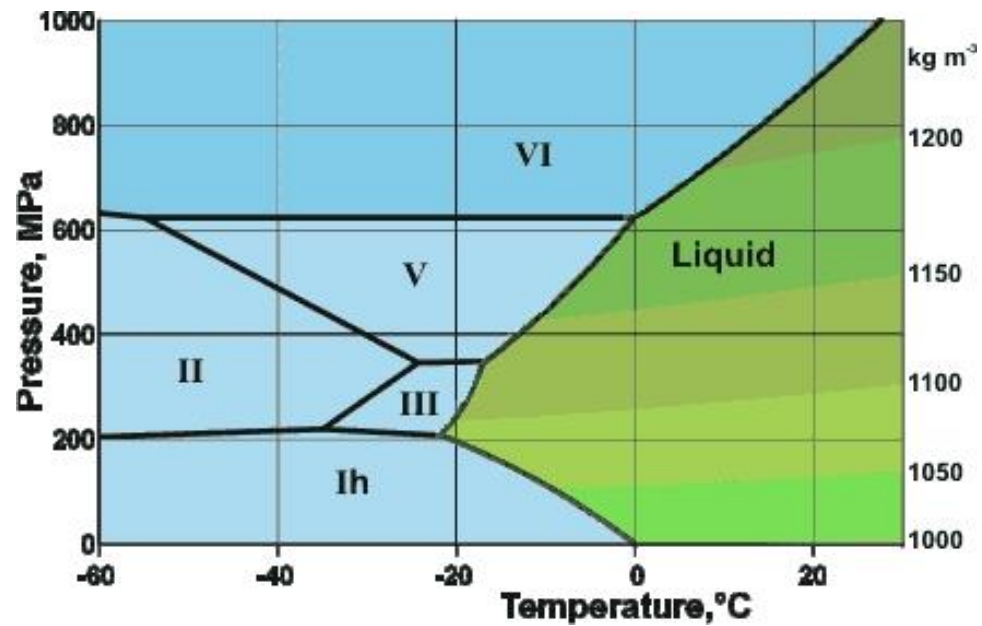
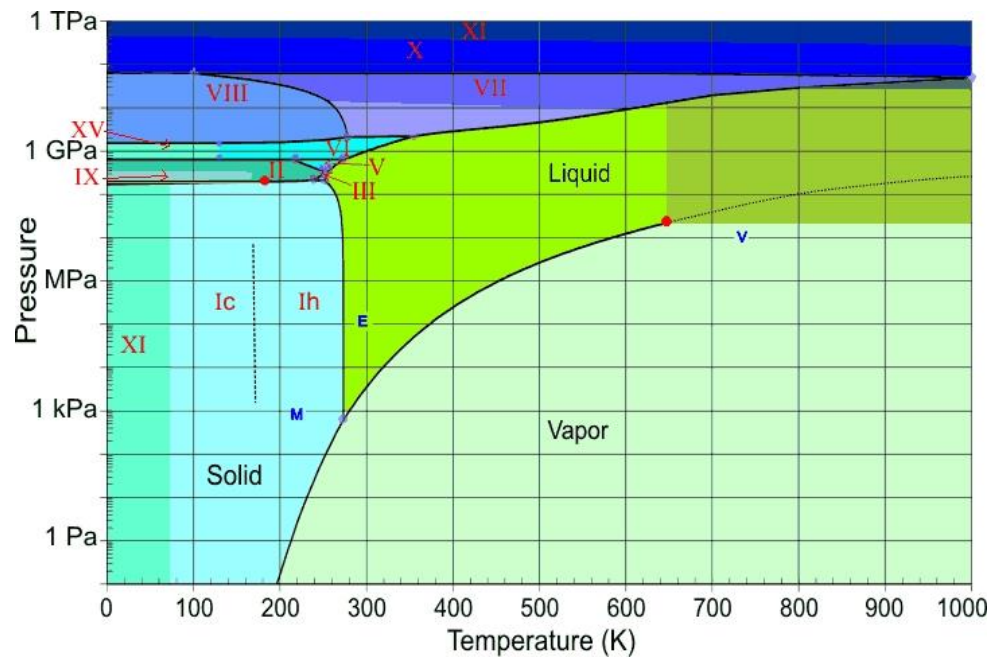
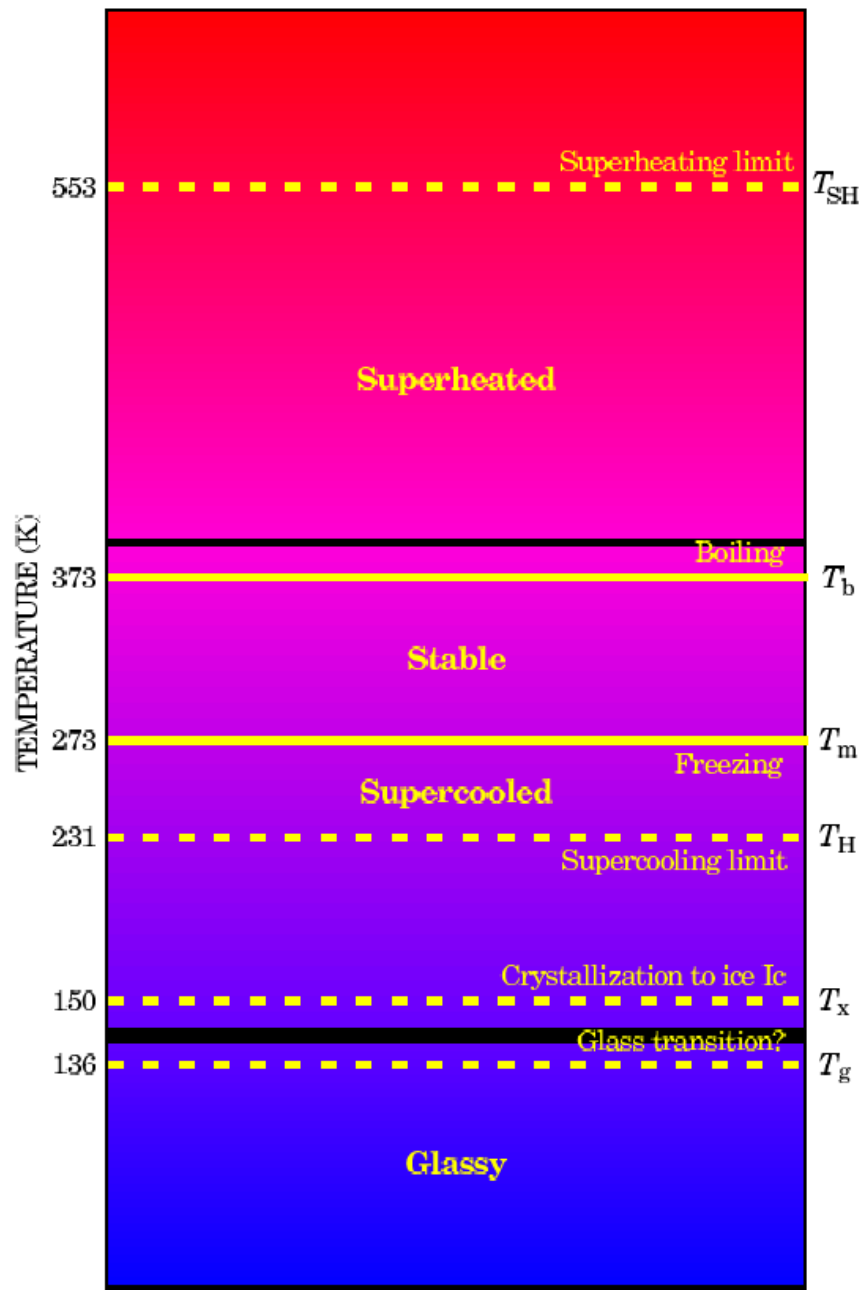
- 什么是热学？关于热现象的研究。

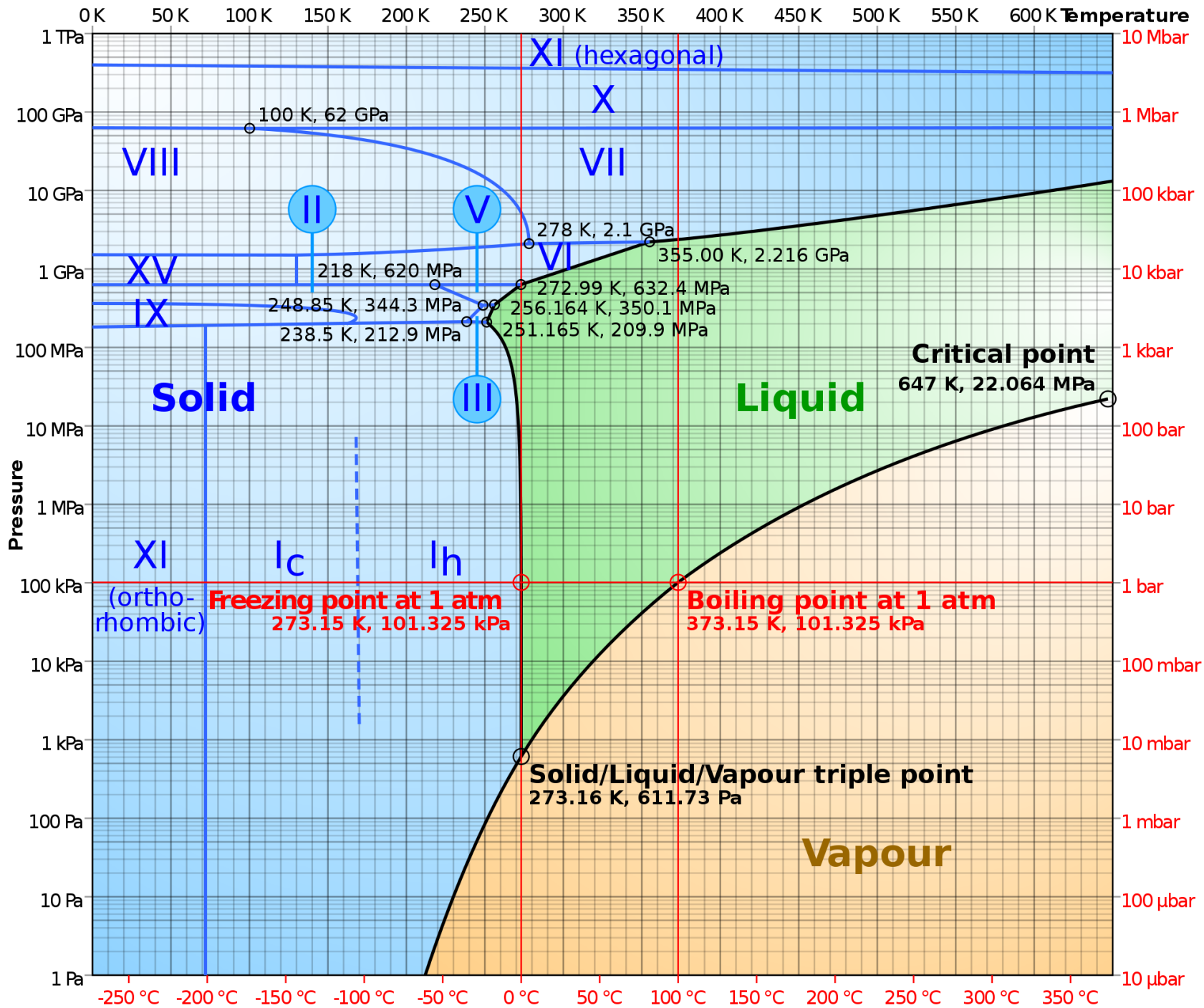


热现象



加热一块未名湖的冰会发生什么？





热学的研究对象

热现象
热运动

和温度有
关的现象

大量粒
子组成
的系统

10^{23}

和大量微观粒子无规则热运动有关的现象



热现象的本质

热动说

热是组成物质的微观粒子运动的表现，热是能量的一种表现形式，可以由其他功转化而来



Rumford

美国,伦福德伯爵,大炮膛孔

培根
胡克
牛顿
笛卡尔

H. Davy
(戴维)
冰摩擦



Joule

英国著名业余科学家，焦耳，400余次，热功当量4.154J/cal



Clausius

克劳修斯，热是分子热运动，论文《关于我们称为热的这种运动》

500B.C.	300B.C.	1600s	1788	1798	1799	1840-1849	1850
		玻意耳?					

四种元素,火、水、土、气
Heracitus(赫拉克利特)

战国, 驸衍, 五行说, 水、火、木、金、土

伽利略
伽桑狄

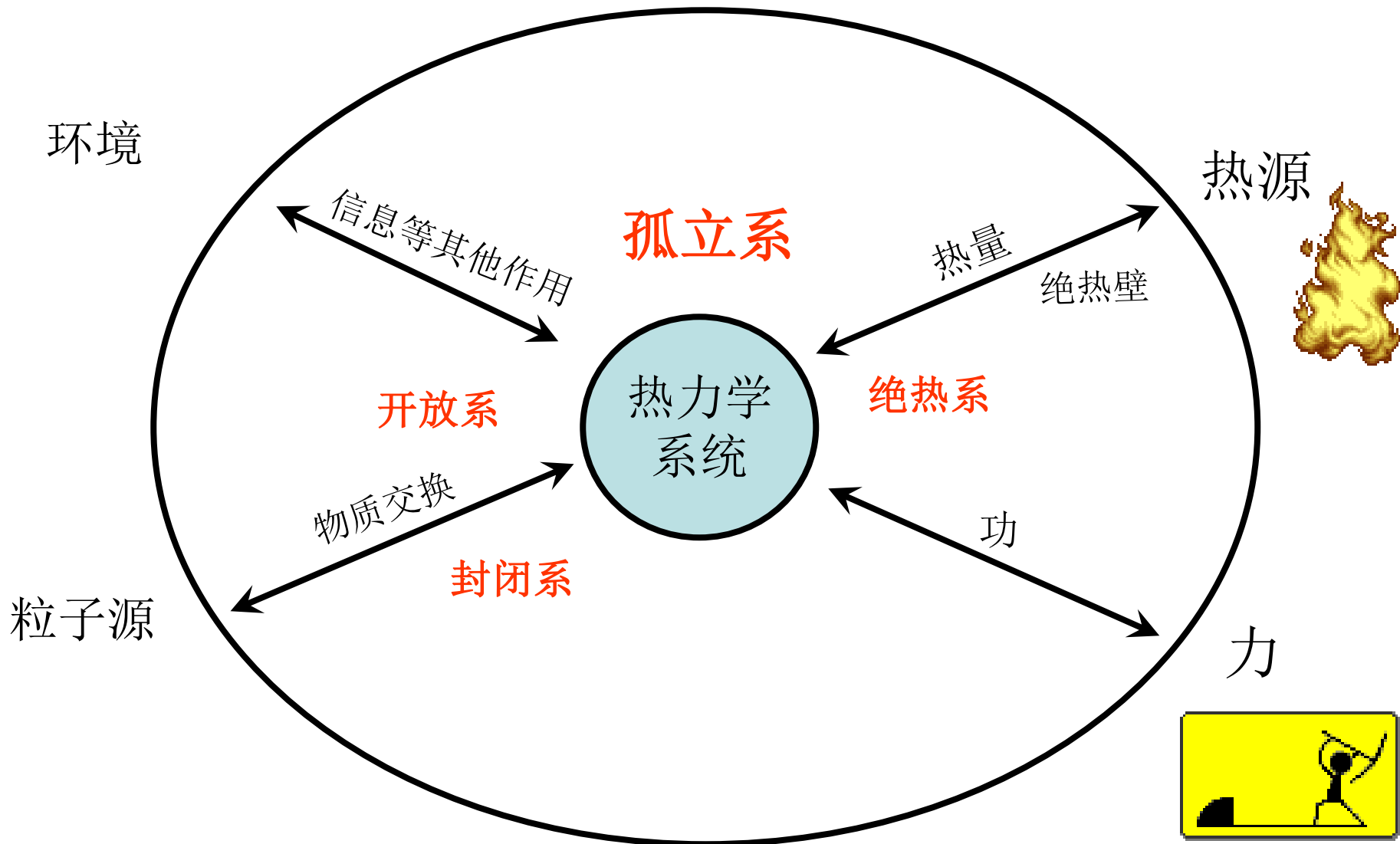
英国,化学兼物理学家
J.Black(布莱克)提出温度、热量概念,完善量热学,提出热量守恒



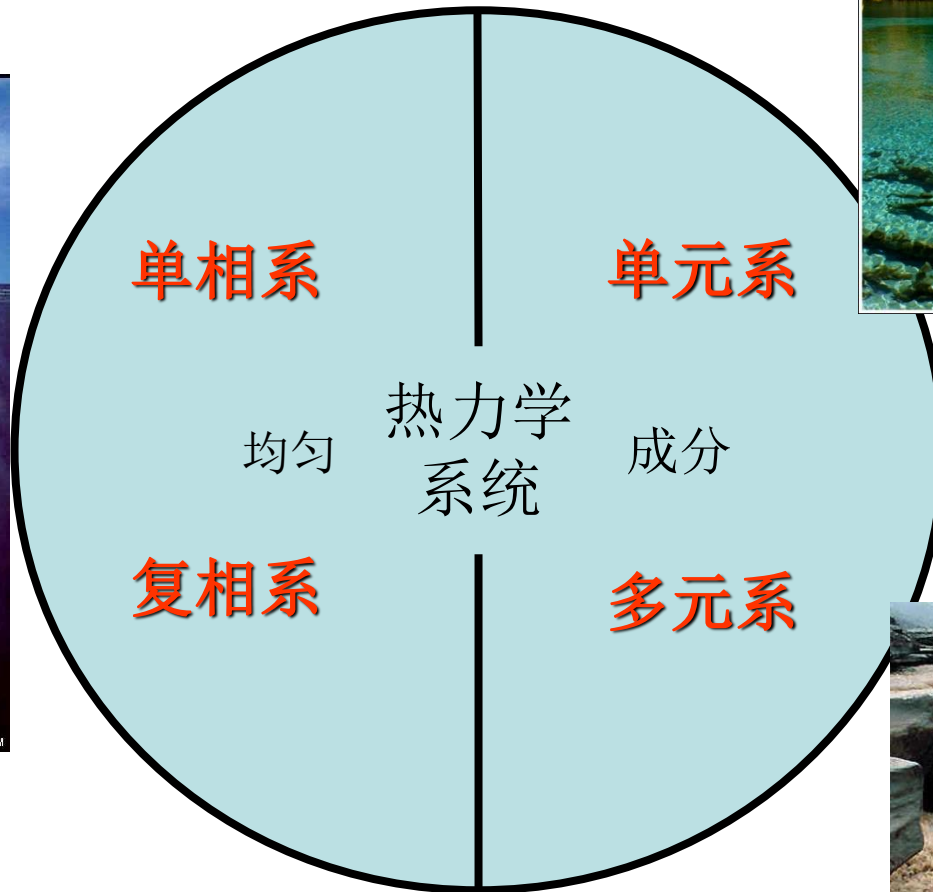
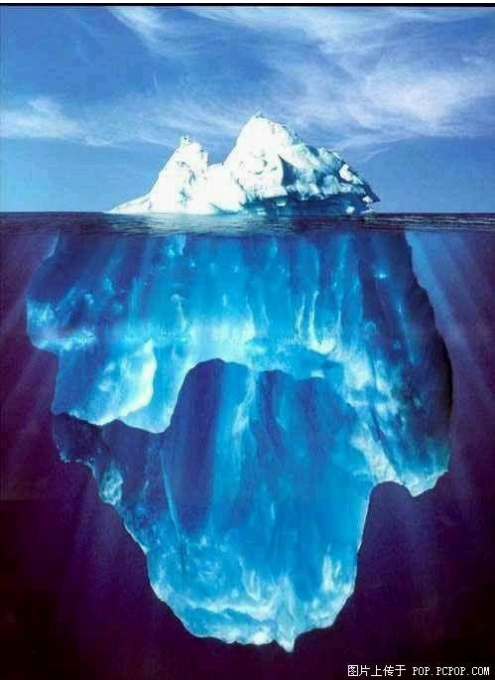
热质说认为热是一种特殊的物质，称之为caloric热质，热质由没有重量的微细粒子组成，可以从一个物体流向另一个物体，其数量守恒

热质说

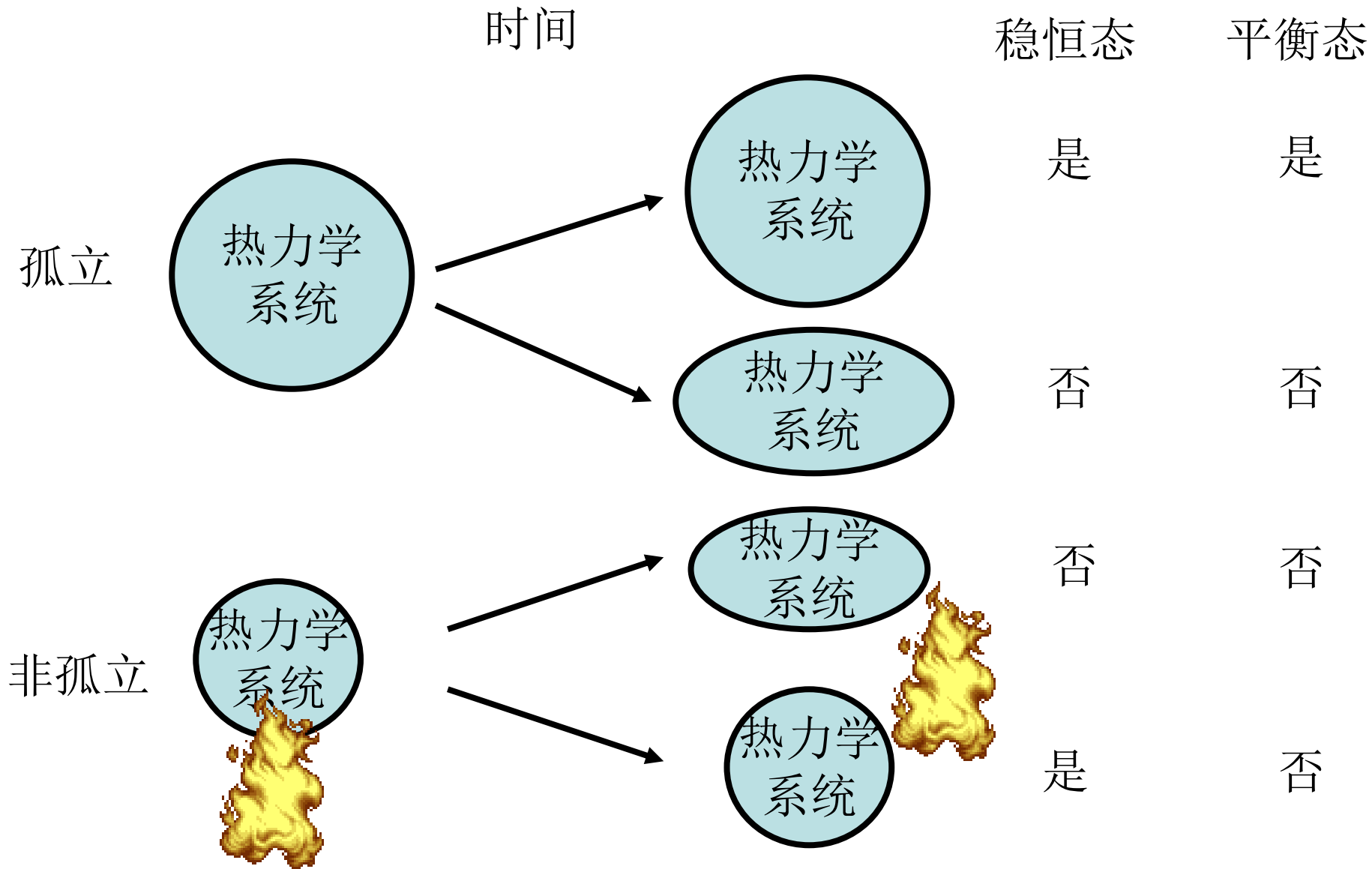
热力学系统



热力学系统



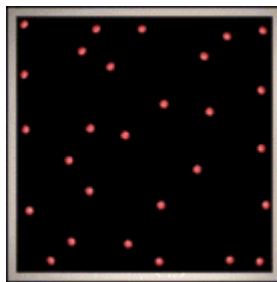
热力学系统



平衡态

微观：动

宏观：静



力学平衡
热平衡
化学平衡

热动平衡

化学反应
化学势

没有外界影响

临界乳光现象
涨落理论

涨落

← 平衡态 →

宏观性质长时间不变

最概然状态



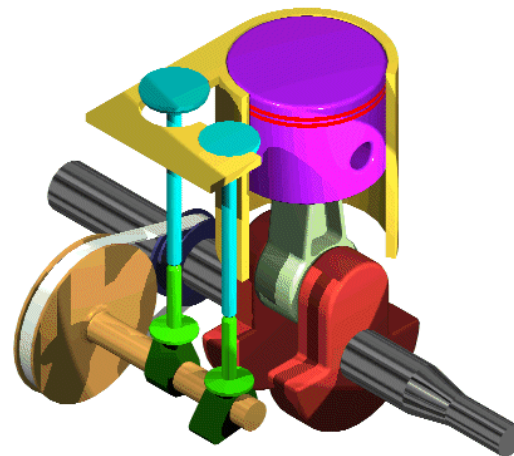
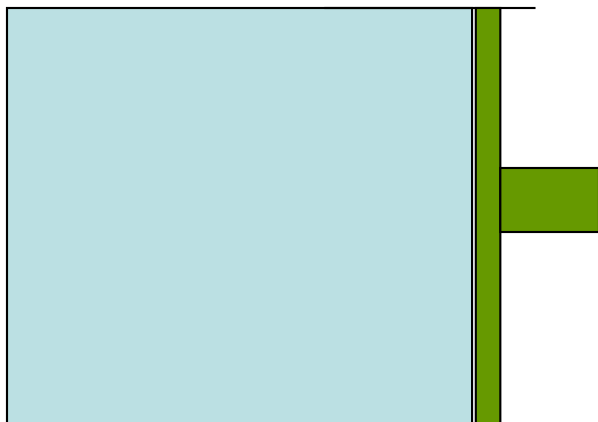
平衡态实际上是一个理想化的概念，因为在实际问题中，不存在完全没有外界影响的系统；

但是如果外界条件的变化速率相对于系统自身由非平衡态趋向于平衡态的速率(弛豫)足够缓慢的话，平衡态的概念就是实际情况的一个合理的抽象和近似。

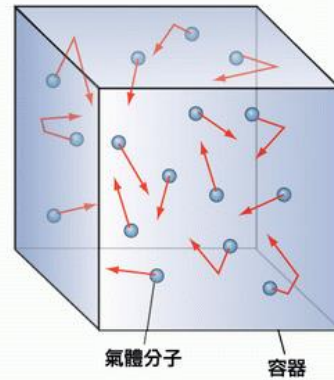
平衡态

气缸中气体达到平衡态的弛豫时间量级为平均碰撞时间 **10^{-9} 秒**

活塞运动一次时间为 **10^{-4} 分钟**



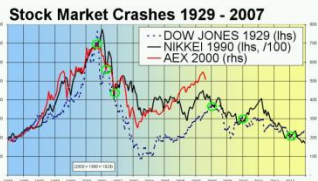
最简单的研究对象



孤立的
单元的
单相的
处于平衡态的
系统



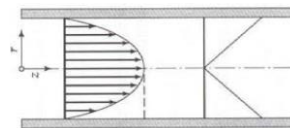
气体中的运输过程



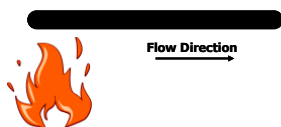
非平衡态 → 近平衡态 → 运输过程

偏离平衡态不远的系统

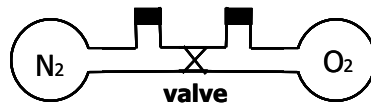
局域平衡假设，即假设系统由一系列达到平衡态的微元组成，对整个系统的描述就是由对每一个平衡态微元的描述而组成的



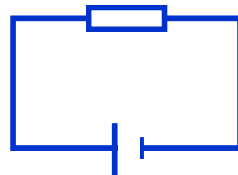
粘滞现象



热传导现象



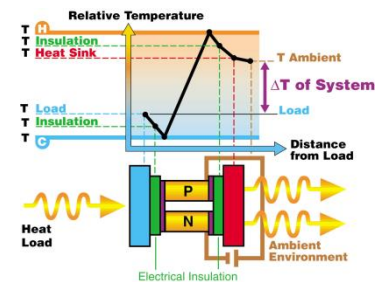
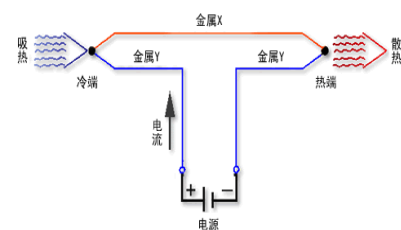
扩散现象



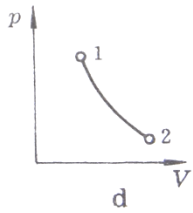
电流

Direct and Coupled Transport Phenomena

	TEMPERATURE GRADIENT	PRESSURE GRADIENT	CHEM. POTENTIAL GRADIENT
HEAT FLUX	Thermal Conductivity	Thermal Filtration (Condensation/evaporation) <small>small</small>	Dufour Effect <small>small</small>
FLUID FLUX	Thermal Osmosis (Vapor transport)	Pressure Advection (Saturated & unsat. hydraulic conduct.)	Osmotic Flow (Osmotic efficiency) (Vapor transport)
SALT FLUX	Soret Effect <small>small</small>	Hyperfiltration (Reverse osmosis) (Osmotic efficiency)	Chemical Diffusion



热力学过程



进行的足够缓慢，以至于系统连续经过的每个中间态都可近似地看成平衡态的过程

平衡态
不随时间变化
不与外界发生相互作用

一个系统由某一状态出发，经过某一过程达到另一状态，如果存在另一过程，它能使系统和外界完全复原（即系统回到原来的状态，同时消除了系统对外界引起的一切影响），则原来的过程称为可逆过程；反之，如果用任何方法都不可能使系统和外界完全复原，则原来的过程称为不可逆过程；

无摩擦的准静态过程是可逆过程

准静态过程
quasi-steady process

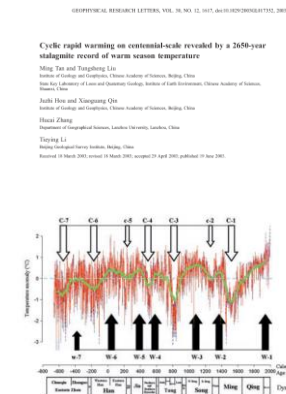
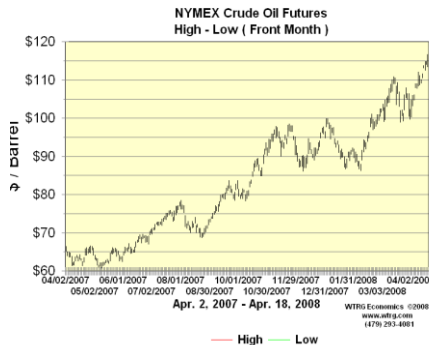
热力学过程
随时间**变化**
与外界发生相互作用

可逆过程
reversible process

原子弹爆炸

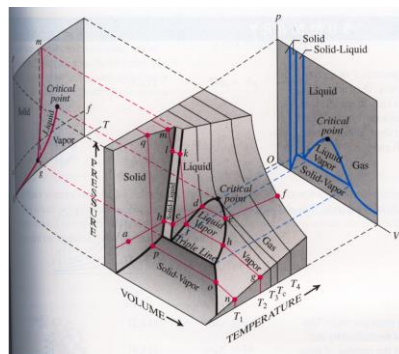
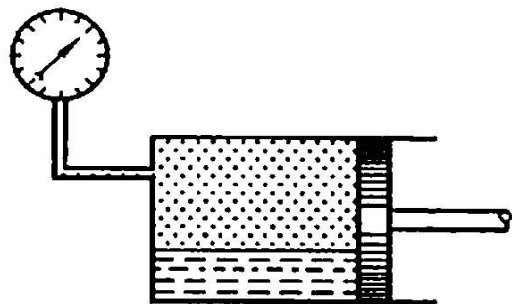
不可再生资源

全球气候变暖



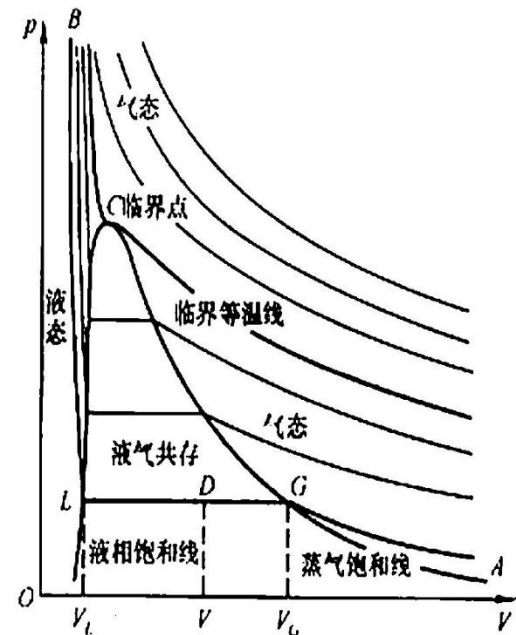
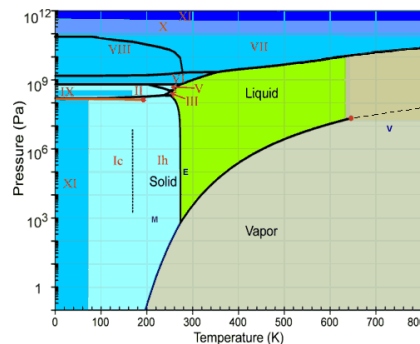
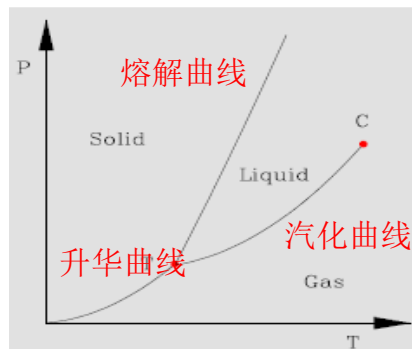
相变现象及其实验规律

等温压缩实验



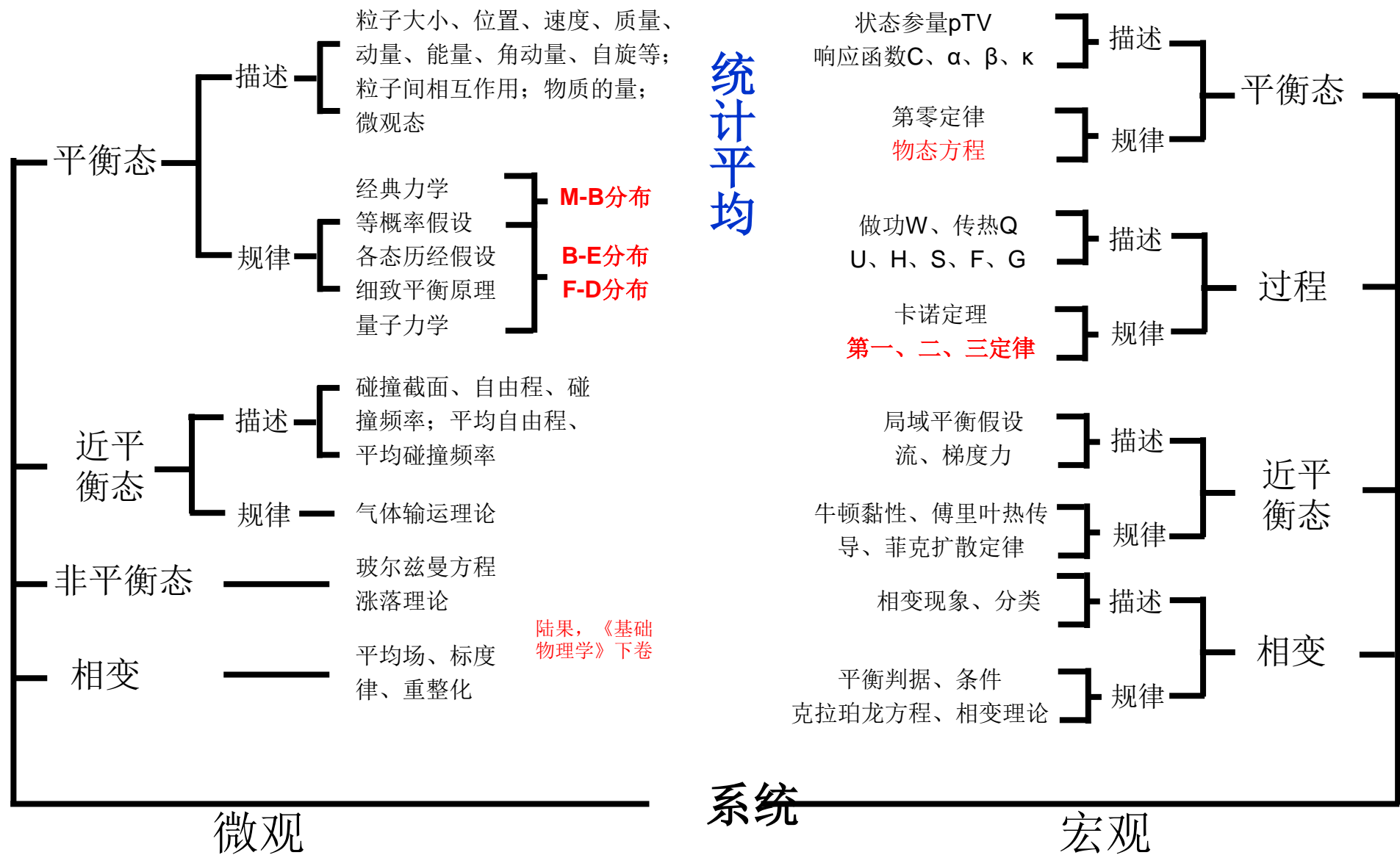
18.23 A pVT -surface for a substance that expands on melting. Projections of the boundaries on the pT - and pV -planes are also shown.

- 1, 从 p - T 图上看, 发生相变时, p 和 T 满足特定的关系, 而与体积无关(从 p - V 图上看相变只发生在一定的体积区间内), 所以发生相变时独立状态参量只有一个。
- 2, 一般说来, 物质从固体变为液体, 从液体变为气体, 体积都会膨胀(一个特例是水变成冰体积会增大), 或者说**体积发生变化**。
- 3, 物质发生相变时通常会吸放热量, 比如等温过程中, 压缩蒸气凝聚成水时, 要放出热量, 这些被统称为**相变潜热**。
- 4, **临界点**处体积气液两相体积连续变化、没有相变潜热(熵连续变化)、有临界乳光现象



热学内容简介

统计平均



热学的研究方法和研究结论

热力学三定律，耗散结构理论等

热力学

普里高津学派耗散结构理论，哈根学派(Haken)协同学，解释非平衡热力学的非线性理论

昂萨格、卡西米尔、普里高津、德格鲁特等人发展了非平衡态热力学的线形理论

克劳修斯《论热的动力理论的主要方程的各种应用形式》

汤姆孙《论热的动力理论》等三篇论文

克劳修斯《论热的动力和由此得出的热学定律》

亥姆霍兹《论力的守恒》

迈耶《论无机界的力》

焦耳热功当量

卡诺定理《关于热的动力的思考》

宏观	1824	1840-1849	1842	1847	1850	1851	1865	1930s-40s	1960s-70s
微观	1857	1858	1866	1877	1902	1924-25	1926-27	1927	

...

John von Neumann, mathematical foundations of quantum mechanics 量子统计力学

费米、狄拉克统计

玻色、爱因斯坦统计

吉布斯《统计力学基本原理》,统计系综理论

玻尔兹曼《关于热动力学第二定律与概率的关系、或热平衡定律》

麦克斯韦《气体的动力理论》

克劳修斯《关于气体分子运动的平均自由程》

克劳修斯发表了一篇非常重要的论文《论我们称之为热的运动》

统计物理学

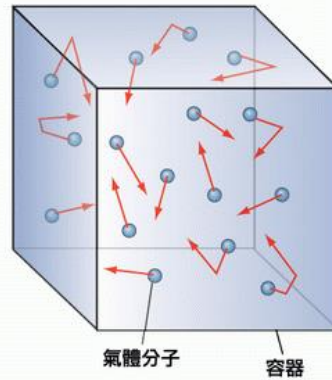
平衡态统计理论、非平衡态统计理论、涨落理论

第零定律和温度

作业

- 1.8, 1.10

我们的研究对象



孤立的
单元的
单相的
处于平衡态的
系统

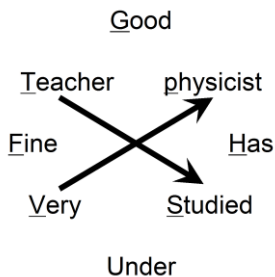


状态参量

无记忆性

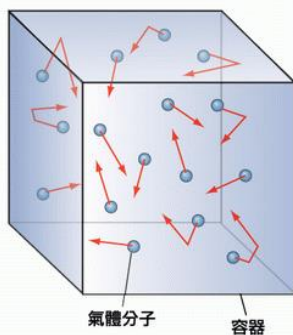
熵S
内能U
焓H
自由能F
吉布斯函数G

温度T
压强p
体积V



处于平衡态的系统，其宏观性质不随时间变化，从而相应描述该系统的可观测测量有确定的数值和意义

宏观状态参量

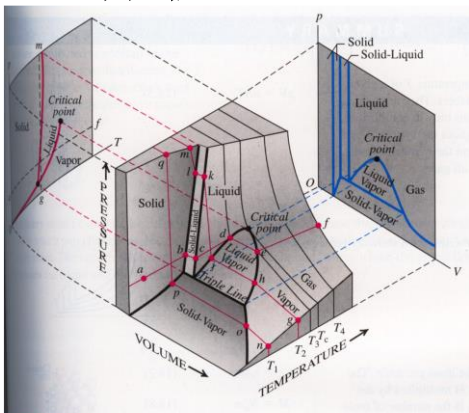


体膨胀系数 $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

相对压力系数 $\beta = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V$

响应函数

等温压缩系数 $K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$

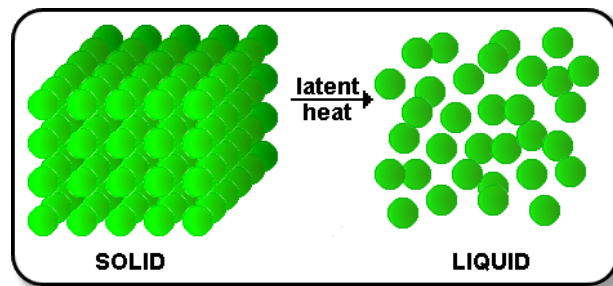


18.23 A pVT-surface for a substance that expands on melting. Projections of the boundaries on the pT- and pV-planes are also shown.

物态方程

$$f(T, p, V) = 0$$

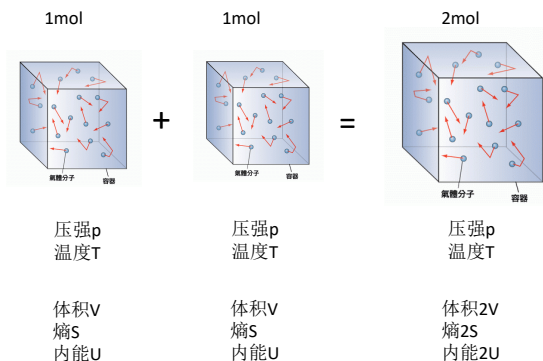
态函数



$$C = \frac{dQ}{dT}$$

宏观状态参量的分类

- 宏观状态参量按照随系统大小变化的性质分为两类，**强度量**和**广延量**。当系统的大小改变时，广延量的值必然发生变化，而强度量则不变。

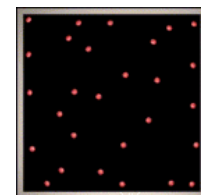


- 需要注意的是广延量通过适当的定义也可以变成强度量，通常是将广延量除以物质的量。
- 而按照状态参量的本身性质，可以分为几何参量、力学参量、化学参量、电磁参量以及热学特有的**热学参量—温度**。

	备注	广延量	强度量	几何	力学	化学	电磁	热学
熵S	$S = k \ln W$ $dS = \frac{\delta Q}{T}$	√						
温度T			√					√
体积V		√		√				
压强p			√		√			
物质的量		√				√		
摩尔质量			√			√		
电场强度E			√				√	
磁场强度H			√				√	
极化强度P			√				√	
磁化强度M			√				√	
粒子数N		√				√		
化学势 μ	$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,p}$		√					
内能U	$dU = TdS - pdV$	√						
焓H	$H = U + pV$	√						
亥姆霍兹自由能F	$F = U - TS$	√						
吉布斯函数G	$G = U + pV - TS$	√						

	备注	广延量	强度量	几何	力学	化学	电磁	热学
热容量C	$C = \frac{\delta Q}{dT}$	√						√
体膨胀系数α	$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$		√		√			
相对压力系数β	$\beta = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V$		√		√			
等温压缩系数κ _T	$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$		√		√			

温度 温标 第零定律



寒冬摸铁器
和木器

冷水热水

冷热程度

宏观

微观

分子热
运动剧
烈程度

温度T



炉火纯青



温度标定

1931(?9)
Fowler
第零定律

经验温标

1593
伽利略
验温器

1714
Fahrenheit
华氏温标

1742
Celsius
摄氏温标

1848,1854
Kelvin
热力学温标

? 1940
理想气体温标



空气
气压p
温度

测温物质
测温属性
固定点

水银
体积V
温度t

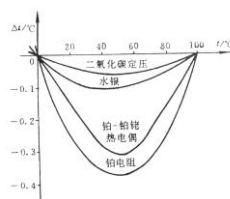
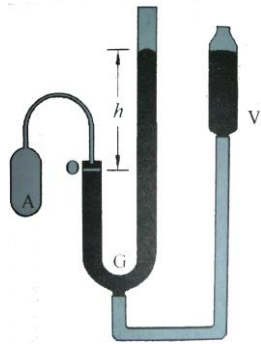


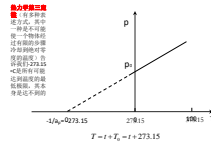
图1-4 以氢定体温度计为标准的校准曲线

理想气体温标



定体气体温度计示意图

$$T = t + T_0 = t + 273.15$$



$$T = T_0 \frac{p}{p_0}$$

$$T = T_0 \lim_{p_0 \rightarrow 0} \frac{p}{p_0}$$

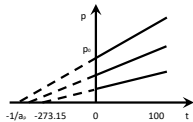


理想气体温标
符号T，单位K

$$p = p_0(1 + a_p t)$$

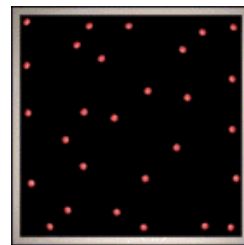
一个标准大气压下水的冰点定为0度，水的沸点定为100度

摄氏温标



$$\lim_{p_0 \rightarrow 0} a_p = \frac{1}{T_0}$$

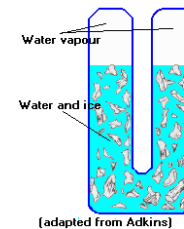
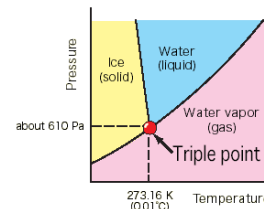
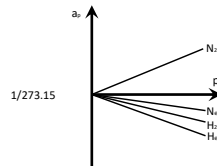
$$T_0 = 273.15^\circ\text{C}$$



Ideal Gas

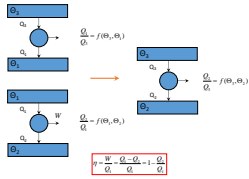


1954年，固定点选为水的三相点， $T_{tr}=273.16\text{K}$



热力学温标

卡诺定理：工作于两个恒定温度之间的一切可逆卡诺热机的效率与**工作物质无关，只是两热源温度的函数。**



以最低温度为零点，称做**绝对温标**，对应温度称做**绝对温度**，现统称**热力学温度**

理想气体温标

热力学温标
开尔文温标

$$\frac{Q_1}{Q_3} = f(\Theta_3, \Theta_1)$$

$$\frac{Q_2}{Q_1} = f(\Theta_1, \Theta_2)$$

$$\frac{Q_2}{Q_3} = f(\Theta_3, \Theta_2)$$

$$f(\Theta_1, \Theta_2) = \frac{Q_2/Q_3}{Q_1/Q_3} = \frac{f(\Theta_3, \Theta_2)}{f(\Theta_3, \Theta_1)}$$

$$\frac{Q_2}{Q_1} = \frac{\psi(\Theta_2)}{\psi(\Theta_1)}$$

$$\psi(\Theta) = \Theta$$

1954年，水的三相点273.16K

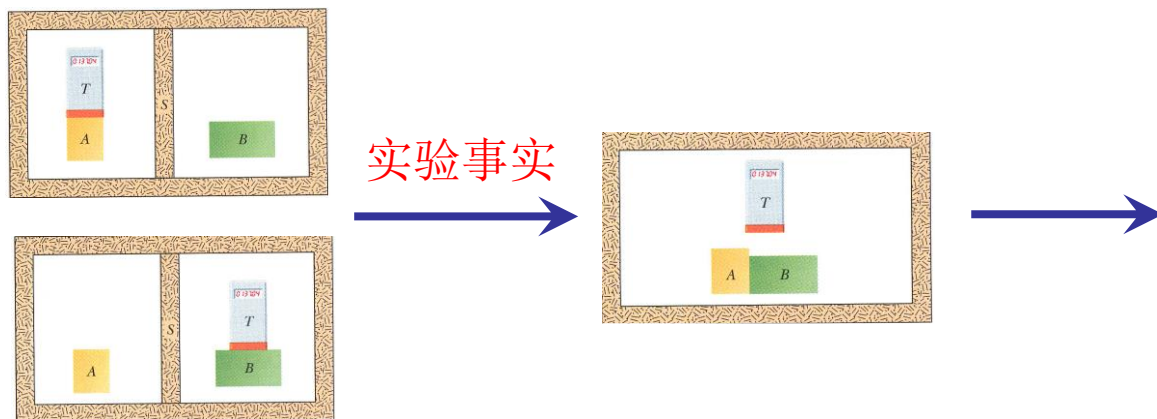
$$\eta = 1 - Q_2/Q_1 = 1 - \Theta_2/\Theta_1$$

$$\eta = 1 - T_2/T_1$$

热力学第零定律

李椿《热学》P26-27

热平衡定律



实验事实

$$T_A = T_C$$

$$T_B = T_C$$

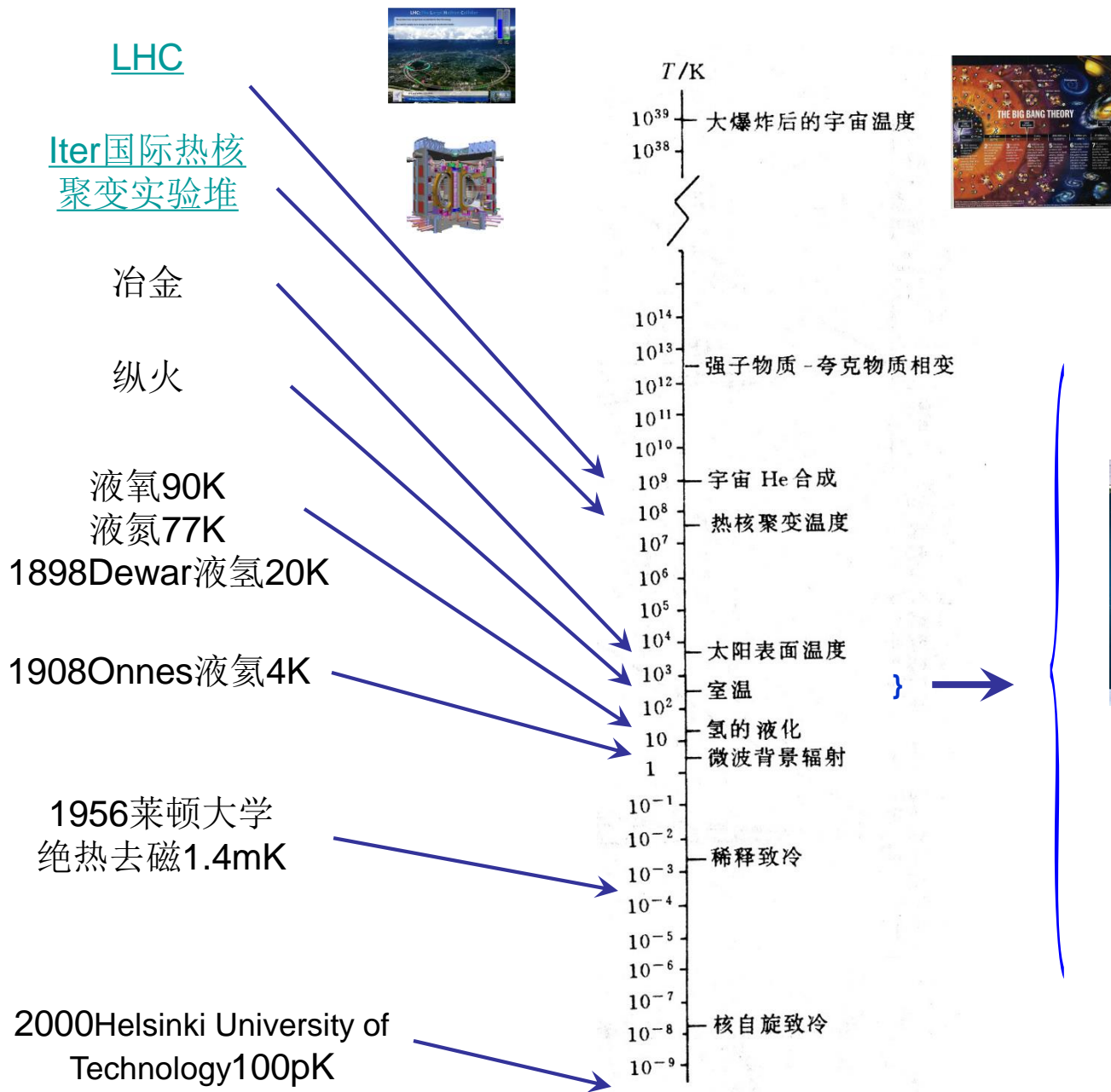


$$T_A = T_B$$

可以用一个温度计去判定不同的物体温度是否相同

互为热平衡的热力学系统具有一个数值相等的状态函数，定义为温度。将A、B作为温度计测量C的温度，则A、B应有相同读数，这就是校准不同温度计的依据。

温度大观



存在着 10^9 种生物大分子



冰河期下降10度，
大批物种灭绝

如果温室效应使得平均气温
升高3度，海平面将上涨2-5
米，迫使10亿人背井离乡

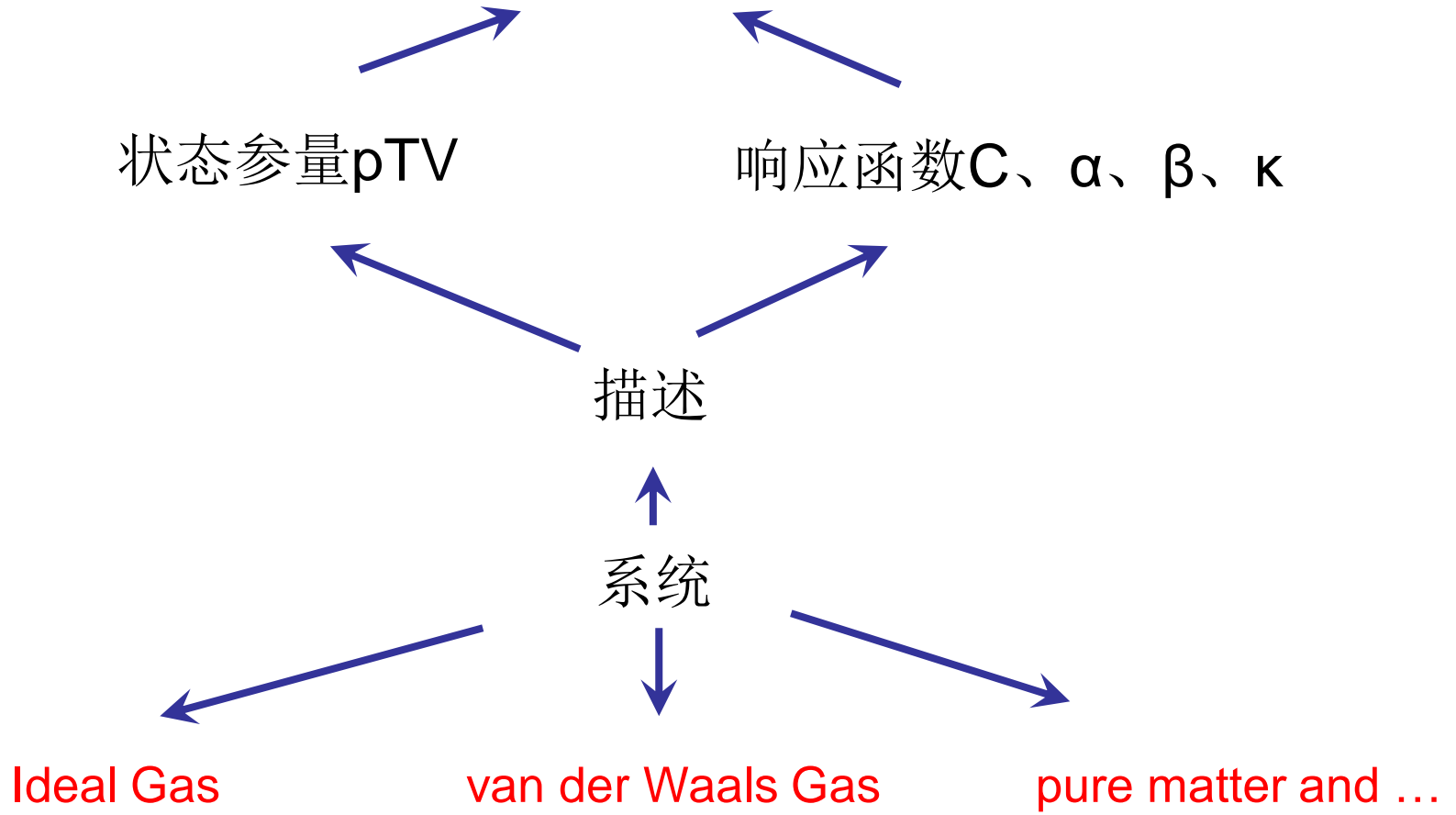
状态方程

作业

- 1.25, 1.32

状态方程(物态方程)

$$f(p, T, V, \dots) = 0$$

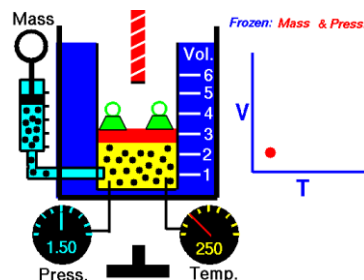


理想气体的物态方程



Boyle's law

$$pV = p_0V_0$$



Charles's law
Gay-Lussac's law

$$V = V_0(1 + \alpha_V t)$$

$$V = V_0 T / T_0$$

标准状况

$$p_0 = 1.01 \times 10^5 \text{ Pa}$$

$$T_0 = 273.15 \text{ K}$$

Avogadro's law

$$V_0 = 22.414 \text{ L}$$

$$\frac{pV}{T} = \frac{p_0V_0}{T_0} = R \quad R = 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Avogadro constant

$$\frac{pV}{T} = \nu R = N \frac{R}{N_A} = Nk_B$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}, k_B = 1.38 \times 10^{-23} \text{ J / K}$$

Avogadro, Amedeo

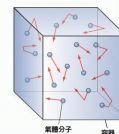
born August 9, 1776, Turin, in the Kingdom of Sardinia and Piedmont; died July 9, 1843, Venice, Italy

Luigi Galvani, Alessandro Volta, Augustin-Louis Lavoisier, and Joseph Priestley were the first to show that oxygen and hydrogen were elements. Lavoisier and Laplace were the first to show that the volume of a gas is proportional to the number of molecules of gas.



pVT

Perfect Gas



Boltzmann constant

$$\alpha_p \rightarrow 1/273.15$$

$$\alpha_V \rightarrow 1/273.15$$

微观模型

例题：由响应函数得到状态方程

$$\alpha = \lim_{\Delta T \rightarrow 0} \frac{1}{V} \left(\frac{\Delta V}{\Delta T} \right)_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

气体 $\alpha = 10^{-3} K^{-1}$
 $\beta = 10^{-3} K^{-1}$

$$\beta = \lim_{\Delta T \rightarrow 0} \frac{1}{p} \left(\frac{\Delta p}{\Delta T} \right)_V = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V$$

$\kappa = 10^0 atm^{-1}$

$$\kappa = \lim_{\Delta p \rightarrow 0} -\frac{1}{V} \left(\frac{\Delta V}{\Delta p} \right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

液体 $\alpha = 10^{-4} K^{-1}$
 $\beta = 10^{1 \sim 2} K^{-1}$
 $\kappa = 10^{-6} atm^{-1}$

$$\alpha = \kappa \beta p$$

$\alpha = 10^{-3} K^{-1}$

固体

$\beta = 10^3 K^{-1}$

$\kappa = 10^{-7} atm^{-1}$



例题：由响应函数得到状态方程

$$p = p(V, T)$$

$$dp = \left(\frac{\partial p}{\partial T} \right)_V dT + \left(\frac{\partial p}{\partial V} \right)_T dV$$

$$= p\beta dT - \frac{1}{V\kappa} dV$$

$$V = V(T, p)$$

$$dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp$$

$$= V\alpha dT - V\kappa dp$$

$$\alpha = 1/T, \quad \beta = 1/T, \quad \kappa = 1/p$$

$$dp = \frac{p}{T} dT - \frac{p}{V} dV$$

$$\frac{dp}{p} = \frac{dT}{T} - \frac{dV}{V}$$

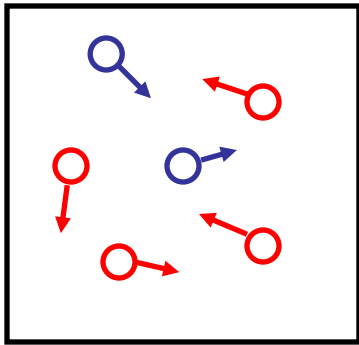
$$d \ln pV = d \ln T$$

$$dV = \frac{V}{T} dT - \frac{V}{p} dp$$

$$\frac{dV}{V} = \frac{dT}{T} - \frac{dp}{p}$$

$$d \ln pV = d \ln T$$

混合理想气体的物态方程



道尔顿分压定律

$$\frac{p_1 V}{T} = \nu_1 R = \frac{m_1}{\mu_1} R = N_1 k_B$$

$$\frac{p_2 V}{T} = \nu_2 R = \frac{m_2}{\mu_2} R = N_2 k_B \quad \longrightarrow$$

$$p = p_1 + p_2$$

混合理想气体状态方程

$$\frac{pV}{T} = \nu R = \frac{m}{\mu} R = N k_B$$

$$\nu = \nu_1 + \nu_2$$

$$N = N_1 + N_2$$

$$m = m_1 + m_2$$

$$\mu = \frac{(m_1 + m_2) \mu_1 \mu_2}{m_1 \mu_2 + m_2 \mu_1}$$

平均摩尔质量

van der Waals Gas and Onnes Equation

Kamerlingh Onnes, Heike

born Sept. 21, 1853, Groningen, Neth. died Feb. 21, 1926, Leiden



Dutch winner of the Nobel Prize for Physics in 1913 for his work on low-temperature physics and his production of liquid helium. He discovered superconductivity, the almost total lack of electrical resistance in certain materials when cooled to a temperature near absolute zero.

From 1871 until 1873 Kamerlingh Onnes studied and worked at Heidelberg University, notably with the German physicists Robert Bunsen and Gustav Kirchhoff. Awarded a doctorate by the University of Groningen (1879), he taught at the Polytechnic School in Delft (1878-1882). From 1882 to 1923 he served as professor of experimental physics at the University of Leiden.



我很高兴把液体氦送给我最尊敬的朋友范德瓦尔斯，是他的理论一直指导了这个气体的液化

Kamerlingh Onnes



Onnes Equation

$$\frac{p}{k_B T} = n + B_2(T)n^2 + B_3(T)n^3 + \dots$$

$n = N/V$ 数密度

位力系数

实际气体

相变

液体

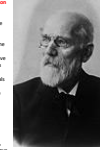
Perfect Gas

$$pV = RT$$

Waals, Johannes Diederik van der

born Nov. 23, 1837, Leiden, Neth. died March 9, 1923, Amsterdam

Dutch physicist, winner of the 1913 Nobel Prize for Physics for his research on the gaseous and liquid states of matter. His work made the study of intermolecular forces and the equation of state possible. A well-educated man with little advantage of the opportunities offered by the University of Leiden, van der Waals first attracted notice in 1857 with his doctoral thesis 'The Continuity of the Liquid and Gaseous States', for which he was awarded a doctorate. In pursuing his research, he knew that the ideal gas law could be derived from the kinetic theory of gases if it could be assumed that gas molecules have zero volume and that there are no attractive forces between them. Being into assumption that neither assumption is correct, in 1882 he introduced into the law two parameters representing size and attraction and worked out a more exact formula, known as the van der Waals equation. Since the parameters were difficult to apply, he considered his work and arrived at an equation (the law of corresponding states) that is the work he is best known for. It was this work that brought him the Nobel Prize and also led to James Clerk Maxwell and Heike Kamerlingh Onnes of the Netherlands to the determination of the necessary data for the liquefaction of hydrogen and helium. Van der Waals was appointed professor of physics at the University of Amsterdam in 1877, spent his retirement until 1907. The van der Waals forces, weak attractive forces between atoms or molecules, were named in his honor.



van der Waals, 1873, doctoral treatise "On the Continuity of the Liquid and Gaseous State"

分子间相互作用
排斥与吸引



Van der Waals Gas

李椿，《热学》，P50-52

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad \left(\pi + \frac{3}{\omega^2}\right)\left(\omega - \frac{1}{3}\right) = \frac{8}{3}\theta$$

$$p_c = \frac{a}{27b^2}, v_c = 3b, T_c = \frac{8a}{27Rb}$$

$$p = \pi p_c, v = \omega v_c, T = \theta T_c$$

范氏对比方程

例题

写出m摩尔范德瓦耳斯气体的状态方程

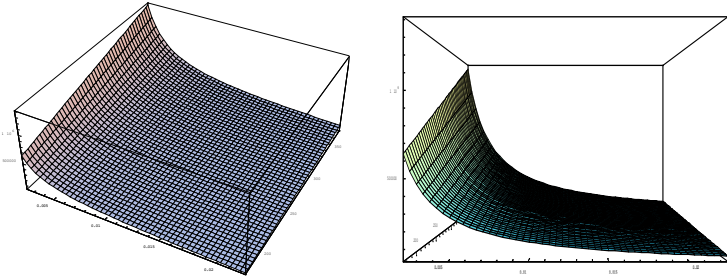
$$\left(p + \frac{m^2 a}{V^2} \right) (V - mb) = mRT$$

将范德瓦耳斯气体状态方程写成昂尼斯方程的形式，
求出其位力系数

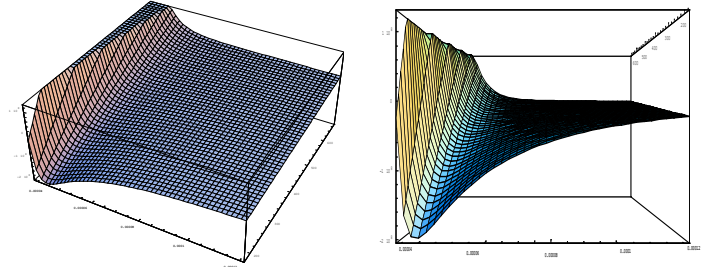
$$\frac{p}{k_B T} = n + \left(\frac{b}{N_A} - \frac{a}{T N_A^2 k_B} \right) n^2 + \frac{b^2}{N_A^2} n^3 + \dots$$

纯物质的pVT图

理想气体



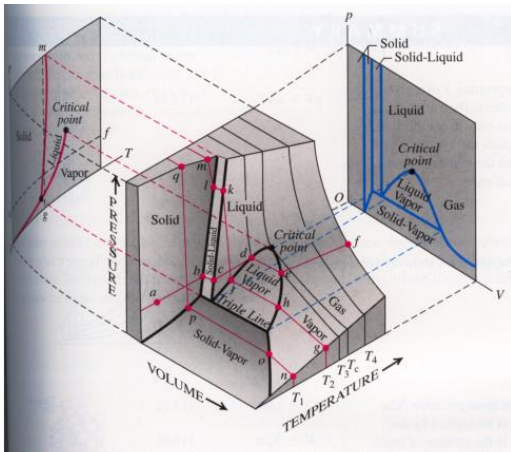
范氏气体



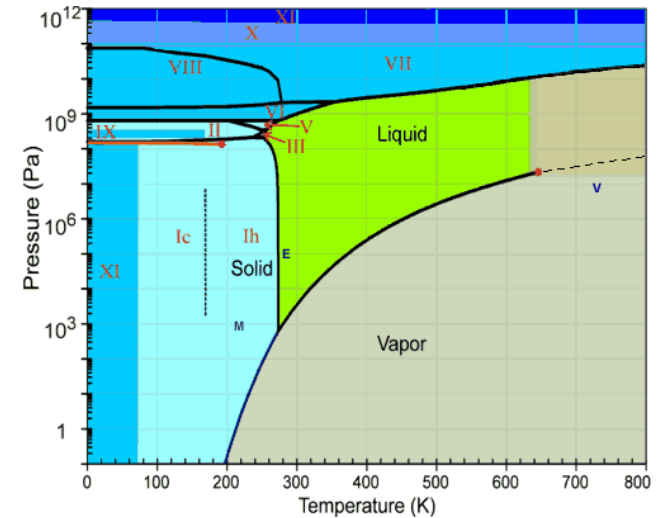
pVT系统



纯物质



18.23 A pVT -surface for a substance that expands on melting. Projections of the boundaries on the surface on the pT - and pV -planes are also shown.



物态方程举例

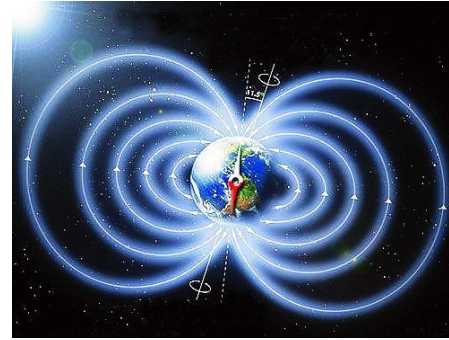
$$F(T, L) = C(T)(L - L_0)$$

胡克定律
金属丝

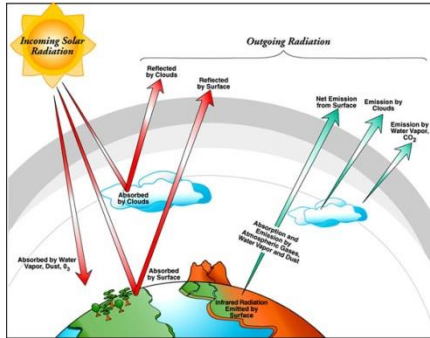


$$M = CH / T$$

居里定律
磁介质



热辐射



电介质

$$p = \frac{a}{3} T^4$$

$$P = (a + b/T)E$$

物质微观图像

作业

- 7.1, 7.3

物质的微观理论—物质结构



Dalton
原子
模型

1800s

Thomson, Sir J.J.
born Dec. 18, 1856, Cheetham Hill, near Manchester, Eng. died Aug. 30, 1940, Cambridge, Cambridgehire

in full Sir Joseph John Thomson English physicist who helped revolutionize the knowledge of atomic structure by his discovery of the electron (1897); he received the Nobel Prize for Physics in 1906 and was knighted in 1908.

“浸入式”原子模型: 认为原子是由带正电的均匀连续体和在其中运动的负电子构成

JJThomson
发现
电子

1897

Rutherford
 α 粒子
轰击氮原子, 发现
质子

1919

海森堡提出
原子核
由中子和
质子构成

1932

高能电子对
核子结构的
探测表明内
部存在更小的
结构, 被
称为部分子

1968



2013 Higgs

LHC

1968--today

Brownian
motion

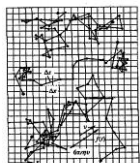
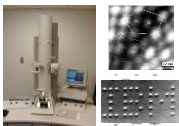


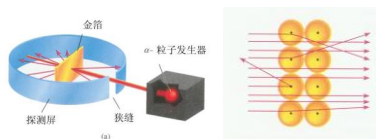
图 3.1.2 布朗运动 (随机性) 布朗运动是悬浮在液体中的微小颗粒 (如花粉) 的无规则运动。图中显示颗粒的一个位置, 两个位置的时间间隔是 30 s。每个网格的分度单位约几微米。

电子显微镜可以直接看到原子



Rutherford
alpha粒子
散射实验

Rutherford alpha粒子散射实验



卢瑟福的
学生查德
威克用质
子轰击铍
核, 发现
中子

量子力学

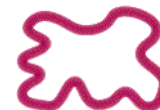
盖尔曼提出
夸克模型,
提出用夸克
来构造各种
粒子



Gell-Mann, Murray

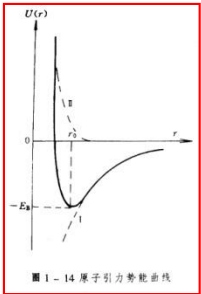
born September 11, 1929, New York, New York, U.S. died August 21, 2019, Los Angeles, California

超对称
超弦



物质的微观理论—相互作用

Building Blocks of Hadron World



Molecules

Atoms

电磁相互作用

Nucleus

Electrons

Proton

Neutron

Hyperons

Mesons

Exotics

(uud)

(udd)

(s...)

(q-q̄)

(qqqq-q̄,...)

强相互作用

弱相互作用

Elementary Particles

Quarks	u up	c charm	t top	Force Carriers
	d down	s strange	b bottom	
Leptons	ν_e electron neutrino	ν_μ muon neutrino	ν_τ tau neutrino	Force Carriers
	e electron	μ muon	τ tau	
	I	II	III	
Three Families of Matter				

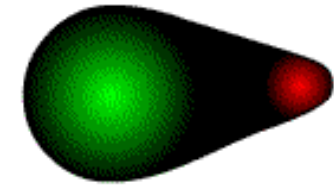
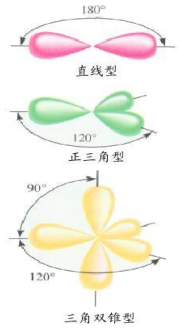
γ
photon

g
gluon

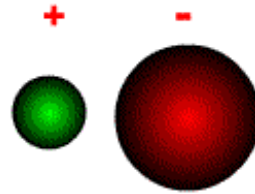
Z
Z boson

W
W boson

物质的微观理论—分子间相互作用



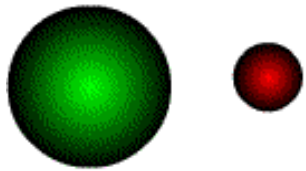
共价键
金属键



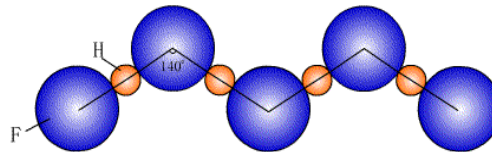
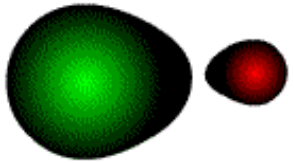
离子键



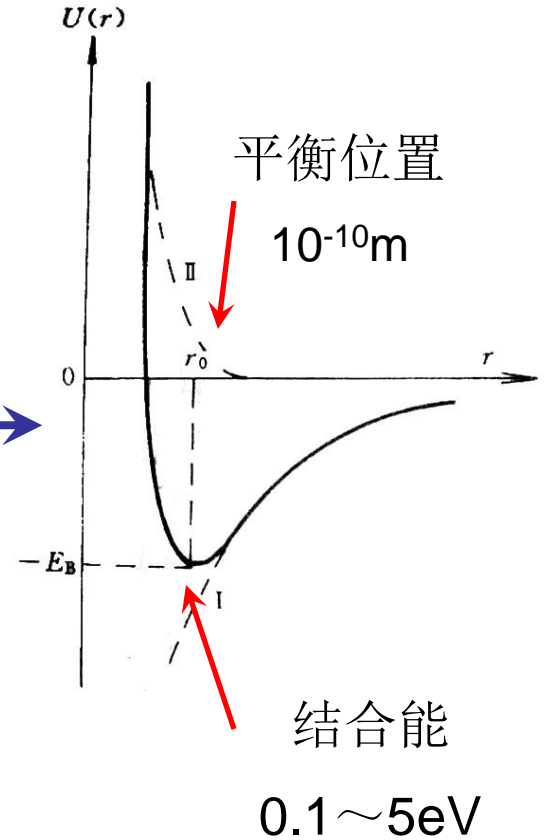
氢键



范德瓦
尔斯键



氢键示意图



分子间相互作用举例，
包科达《热物理学基础》，P44-46

物质的微观理论—分子热运动

爱因斯坦(1905年)和斯莫陆绰斯基(Smoluchowski, 1906年)、郎之万(Langevin, 1908年)关于布朗运动的理论工作, 证明了布朗粒子位移平方的平均值正比于时间t

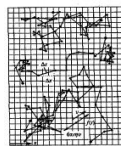
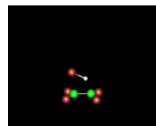
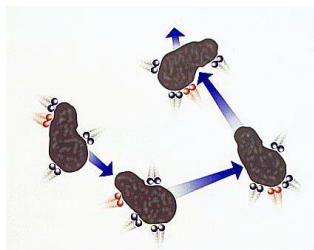


图 2.1.2 布朗粒子(墨粉颗粒)在液体中(图中)的随机运动。图中显示了布朗粒子的一个位置, 并标出了其在时间间隔 Δt 内, 两个相邻时刻的位置 x_1 和 x_2 。

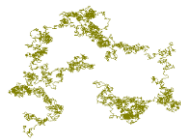


图 2.3: 一个简单布朗运动的粒子向视图。

英国植物学家**布朗**(R. Brown)在显微镜下观察到悬浮在静止液体里的花粉不停地做无规则运动。

$$m \frac{d^2 x}{dt^2} = F(t) - \alpha \frac{dx}{dt}$$

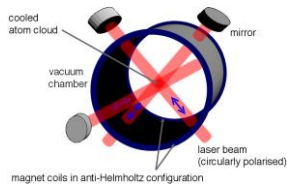
$$m \frac{d^2 x^2}{dt^2} + \alpha \frac{dx^2}{dt} = 2m \left(\frac{dx}{dt} \right)^2 + 2xF(t)$$

$$m \frac{d^2 \overline{x^2}}{dt^2} + \alpha \frac{d\overline{x^2}}{dt} = 2k_B T$$

$$\overline{x^2} \propto Tt, m \rightarrow 0$$

赵凯华新概念《热学》P258-260

cooling and trapping atoms using laser light



Steven Zhu

Steven Chu 李振文
Steven Chu (Chinese: 李振文) is an American physicist and chemist. He is a member of the National Academy of Sciences, the National Academy of Arts, and the American Academy of Arts and Sciences. He is also a member of the Chinese Academy of Sciences. He is a recipient of the Nobel Prize in Physics (1997) for his work on the manipulation of atoms and molecules using laser light. He is currently a professor at Stanford University.

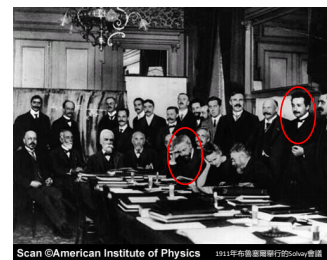
1908年皮兰(Perrin)实验证实

Perrin, Jean
born Sept. 30, 1870, Lille, France died April 17, 1942, New York, N.Y., U.S.

in full: Jean-Baptiste Perrin French physicist who, in his studies of the Brownian motion of minute particles suspended in liquids, established a quantitative measure of the phenomenon and thereby confirmed the atomic nature of matter. For this research he was awarded the Nobel Prize for Physics in 1926. Educated at the Ecole Normale Supérieure, Paris, Perrin joined the faculty of the University of Paris (1908) where he became professor of physical chemistry (1910-40). In 1905 he established that cathode rays are negatively charged particles (electrons). He attempted to determine the mass of these particles when soon superseded by the work of J.J. Thomson.



About 1908 Perrin began to study Brownian motion, the erratic movement of particles suspended in a liquid. Einstein's mathematical analysis (1905) of this phenomenon suggested that the particles were being pushed by the randomly moving water molecules around them. Using the newly developed photomicrographs, Perrin carefully observed the manner of sedimentation of these particles and provided experimental confirmation of Einstein's equations. His observations also enabled him to estimate the size of water molecules and atoms as well as their quantity in a given volume. This was the first time the size of atoms and molecules could be reliably calculated from actual visual observation. Perrin's work helped raise atoms from the status of useful hypothetical objects to observable entities whose reality could no longer be denied.



Scan ©American Institute of Physics 1911年布鲁塞耳举行的索维会议

证实原子存在的人

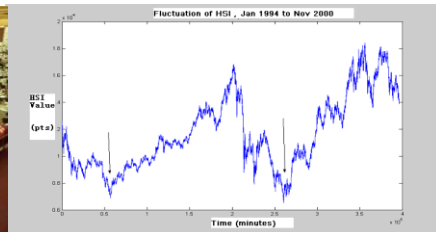
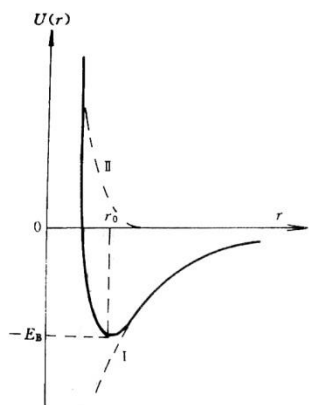


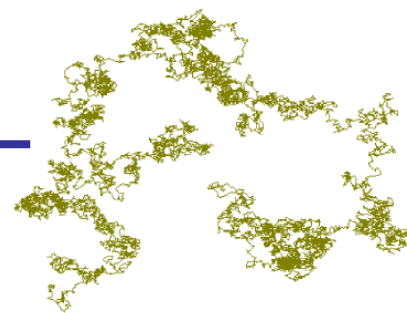
Fig. 1 Fluctuation of HSI during the period Jan. 3, 1994 to Nov. 30, 2000. The period is characterized by the 1995 'bearish market' and the 1997-98 crash.

物质的等离子态? 、气态、液态、固态、超密态（白矮星、中子星、黑洞）



势能 E_p

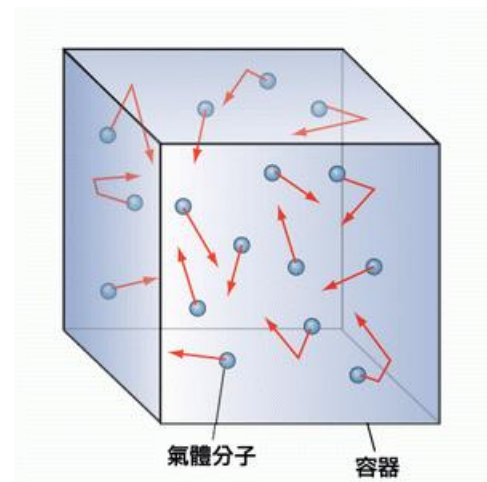
动能 E_k



>

≈

<



物质的气态、固态、液态

- 气体---非凝聚态，分子位置相互间没有关联

直径 10^{-10}m



间距 10^{-9}m



273K时， N_2 平均速率400m/s
 H_2 平均速率1700m/s

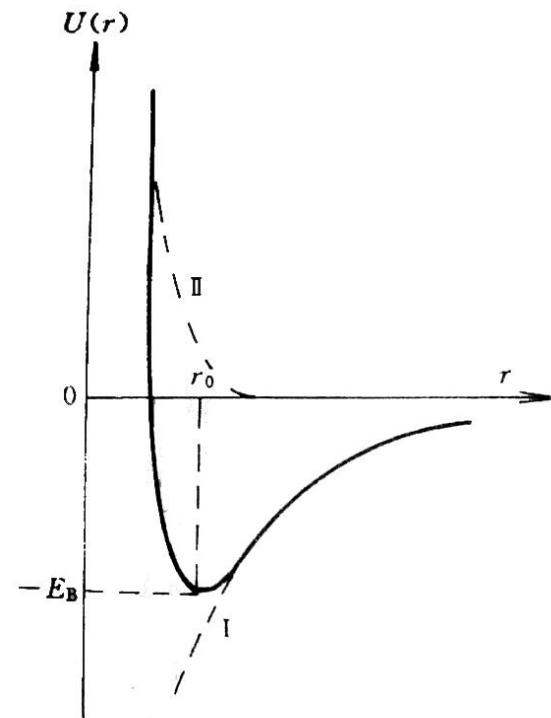
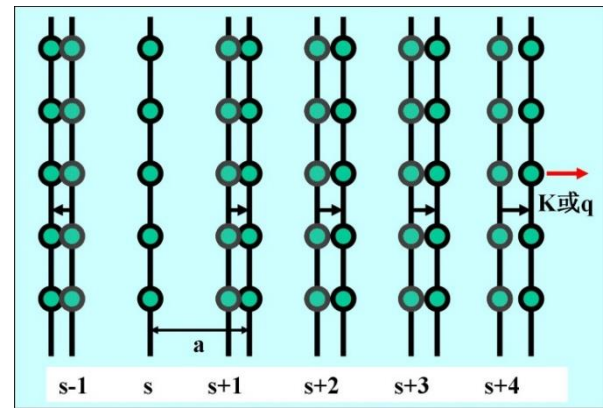
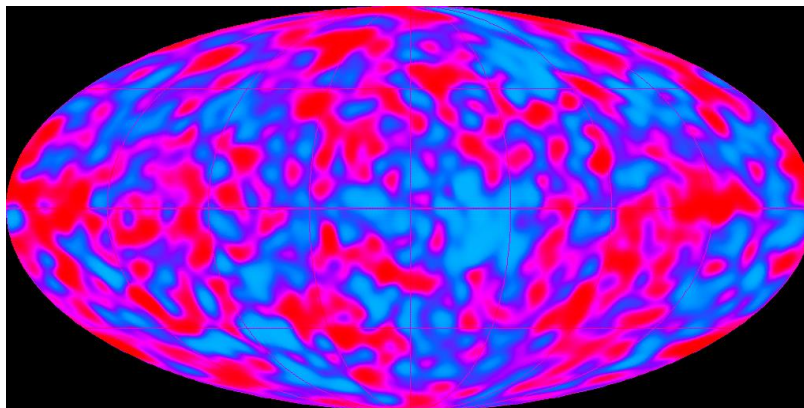
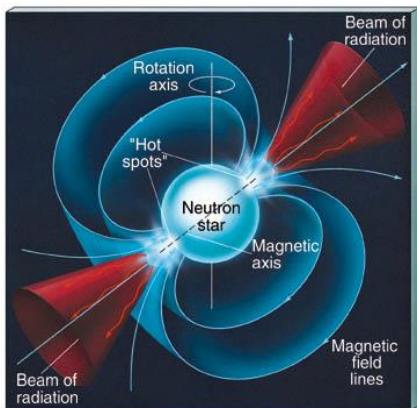
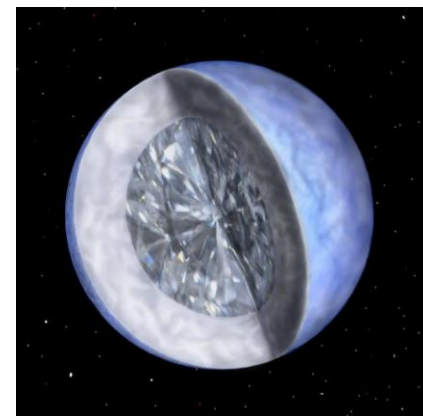
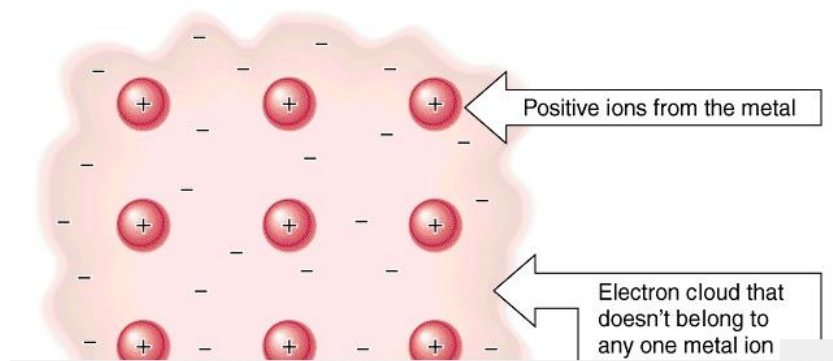


图 1 - 14 原子引力势能曲线

物质的气态、固态、液态

“气体”

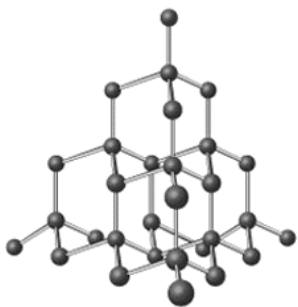
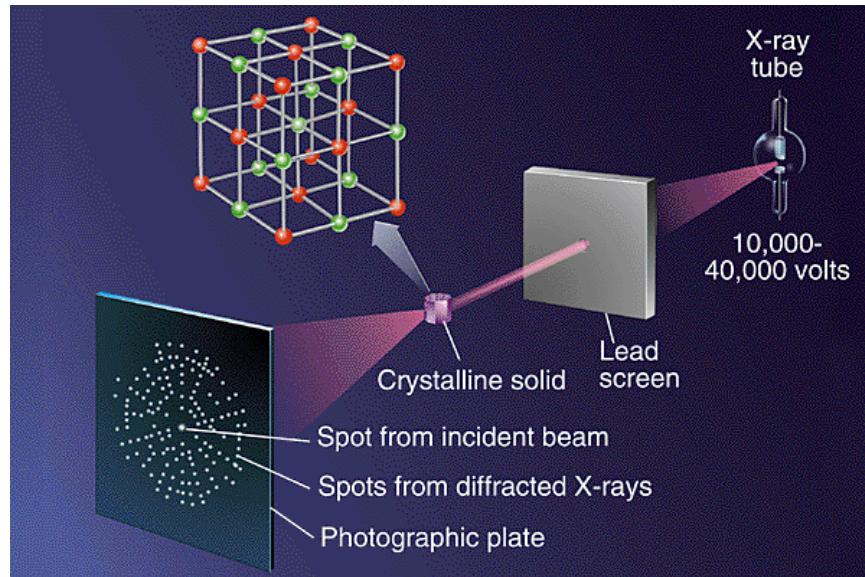
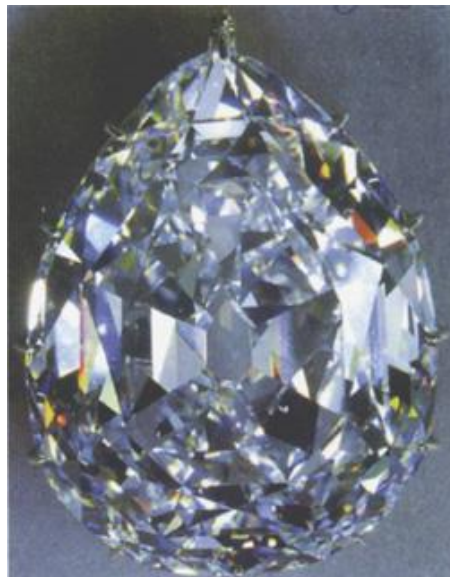
普通气体
电子气体
白矮星
中子星
光子气
固体晶格中的声子气



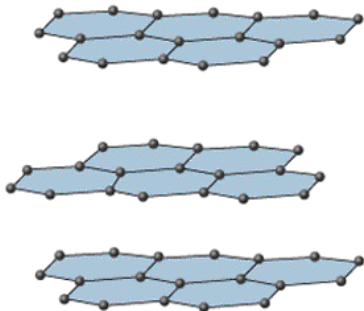
物质的气态、**固态**、液态

完美晶体

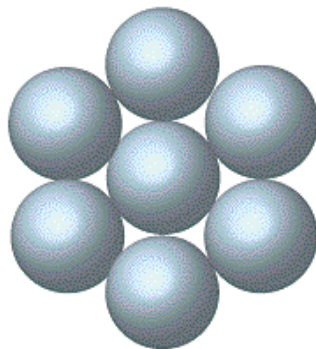
离子键
共价键
金属键
范德瓦耳斯键
氢键



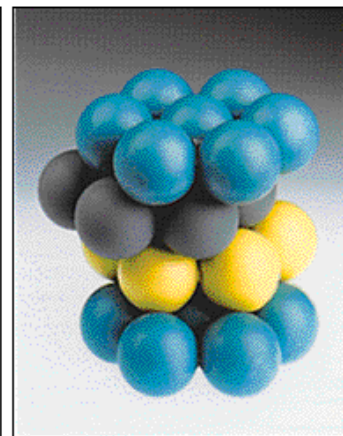
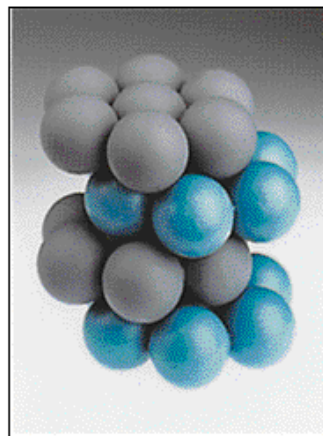
(a) Diamond



(b) Graphite



Close-packed layer of spheres

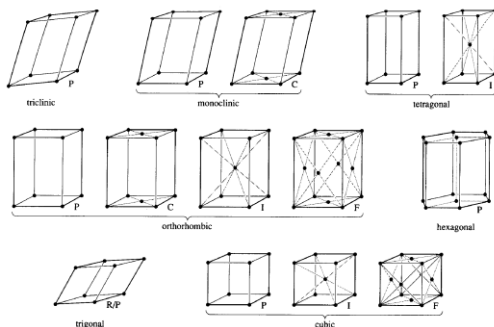
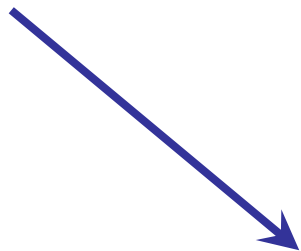


晶体与对称性

旋转, 镜面



32个点群



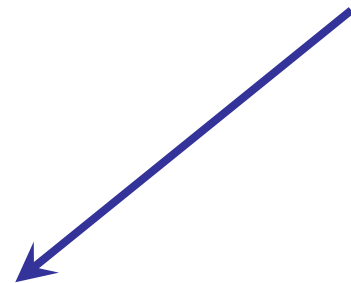
7个晶系14种Bravais格子



平移



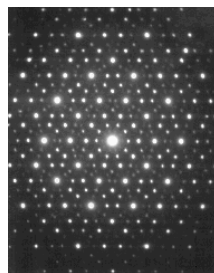
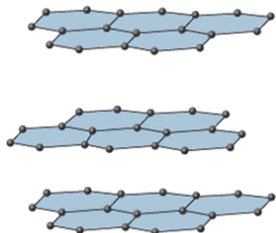
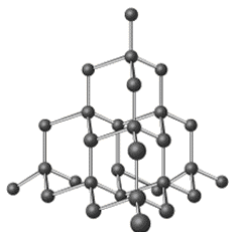
平移群



230个空间群

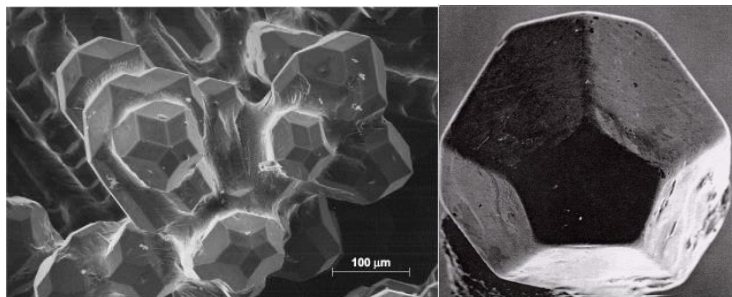
准晶体

完美的晶体只具有1, 2, 3, 4, 6次对称轴

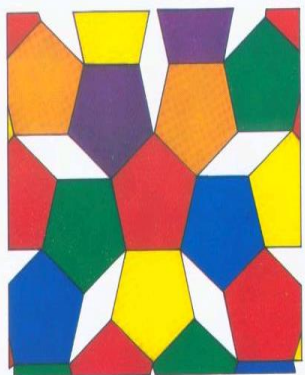


1984年, Shechtman等在寻找既轻又硬的Al合金中,在急冷的Al-Mn合金中获得了具有五重对称,斑点明锐的电子衍射图,定出其点群为 $m\bar{3}5$.

D. Shechtman, I. Blech, D. Gratias, and J.W. Cahn, "Metallic phase with long-range orientational order and no translational symmetry," *Phys. Rev. Lett.* **53** (1984) 1951-1953.



准晶体



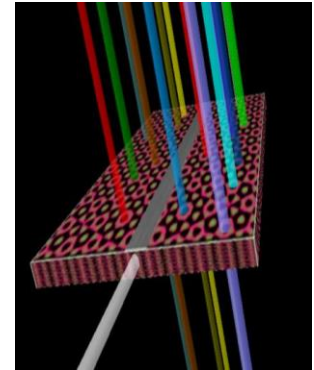
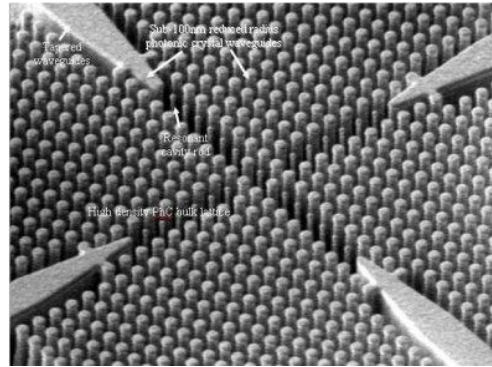
PenrosePattern

郭可信: 五次、八次、十二次对称

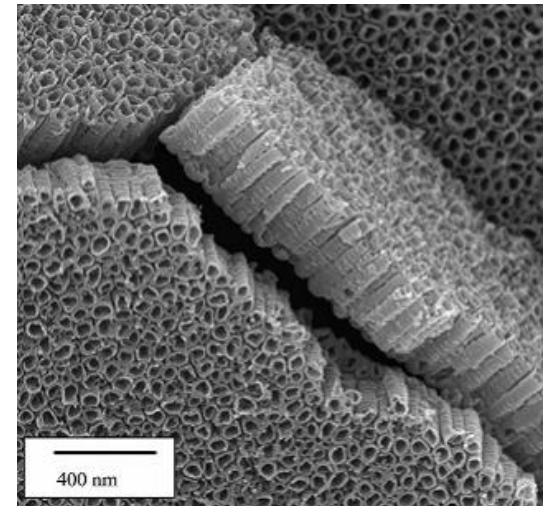
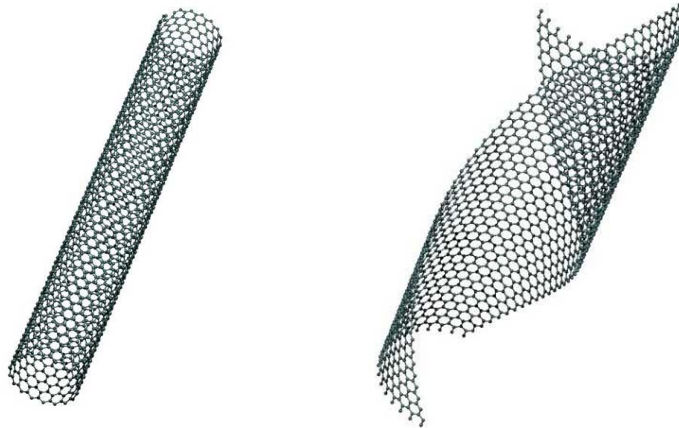


新型晶体

光子晶体



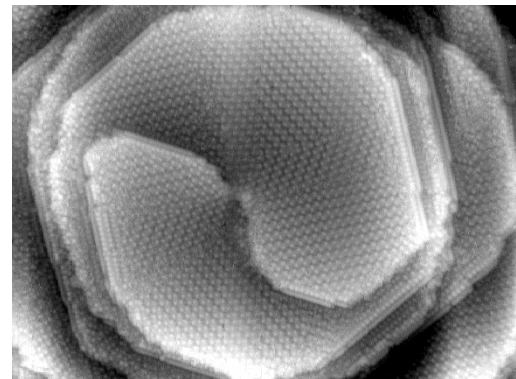
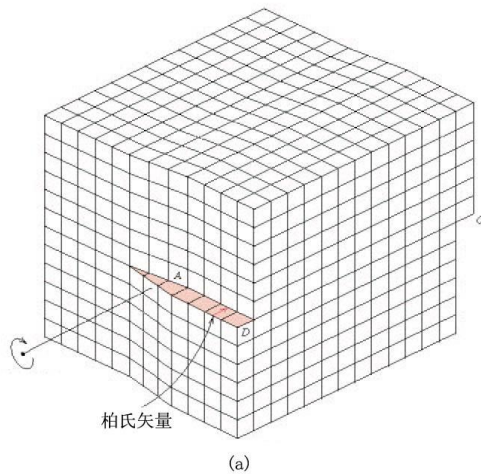
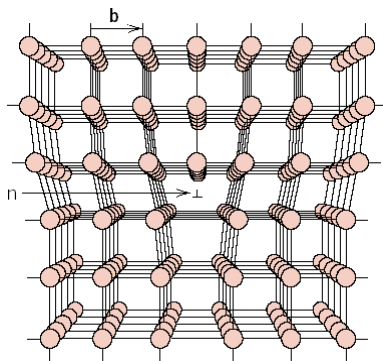
纳米材料



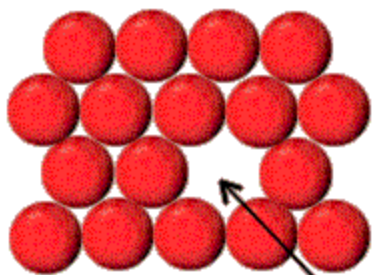
物质的气态、**固态**、液态

晶体中的缺陷

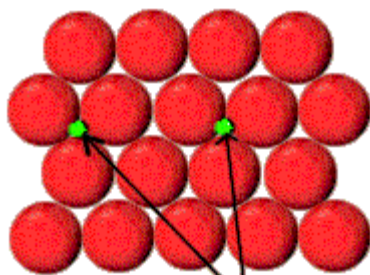
位错



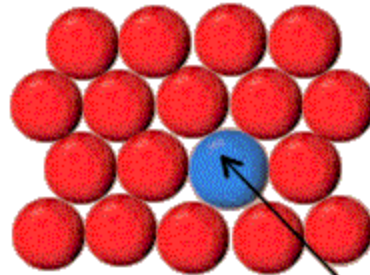
空位
间隙
杂质



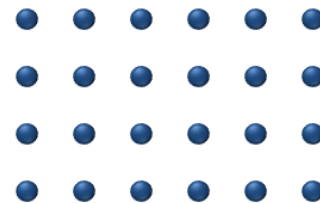
Vacancy



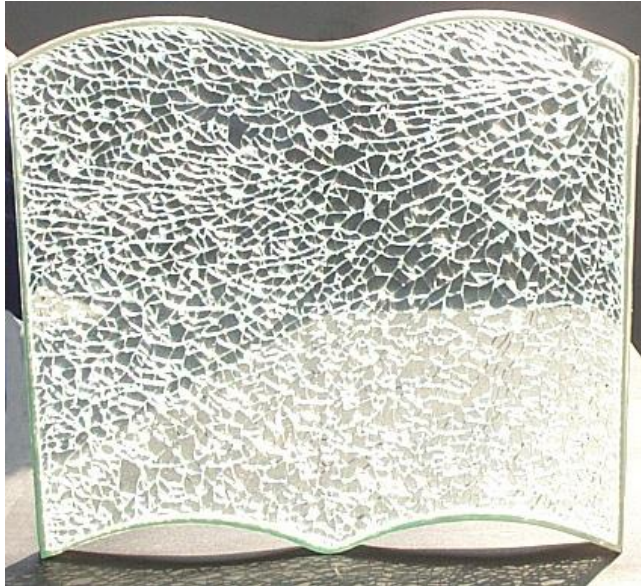
Interstitial Atoms



Substitutional Atom



非晶体



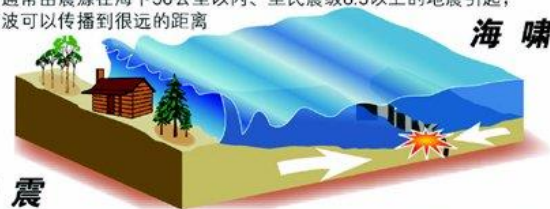
物质的气态、固态、**液态**

液体---稠密的气体



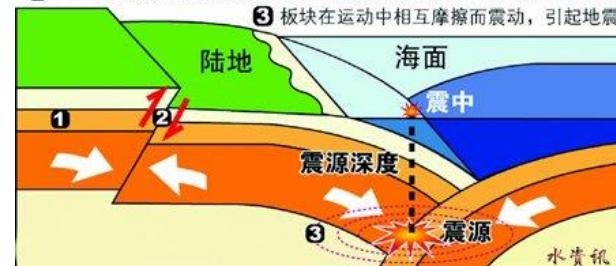
流体

海啸通常由震源在海底50公里以内、里氏震级6.5以上的地震引起，
震荡波可以传播到很远的距离

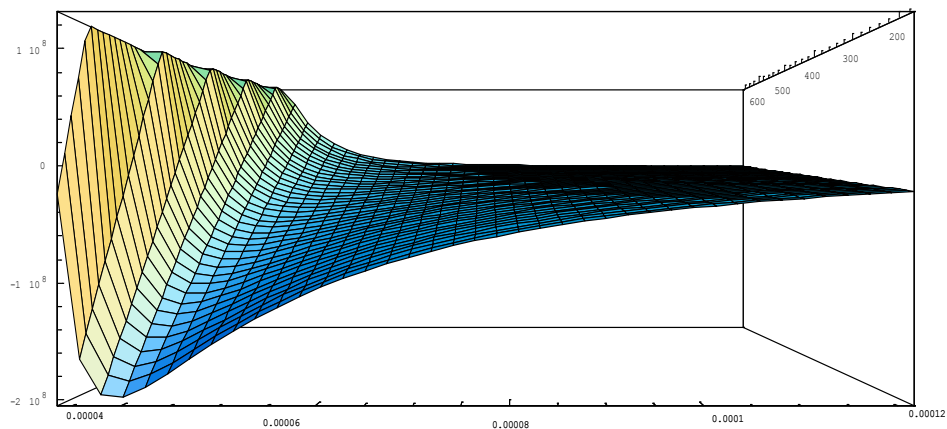


地震

- 1 板块边界运动形态使得板块边界地区的地壳发生弹性变形而产生应力
- 2 一旦超过抵抗它的摩擦阻力时，地壳即会错动反弹至没有应变的位置
- 3 板块在运动中相互摩擦而震动，引起地震



分子间相互作用不可忽略，又不像固体那样紧密束缚，
可以用范德瓦耳斯方程定性描述液体



物质的气态、固态、**液态**

液体---濒临瓦解的晶格

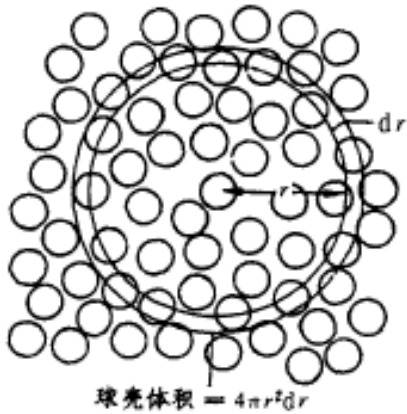


图 1-55 围绕给定中心原子的径向分布

去。如图 1-55 所示,取任一分子为中心,以半径 r 作球面,设此球面上分子的平均数密度为 $n(r)$,则夹在半径为 r 和 $r + dr$ 两球面之间的球壳内分子平均分子数为

$$g(r) dr = 4 \pi r^2 n(r) dr, \quad (1.43)$$

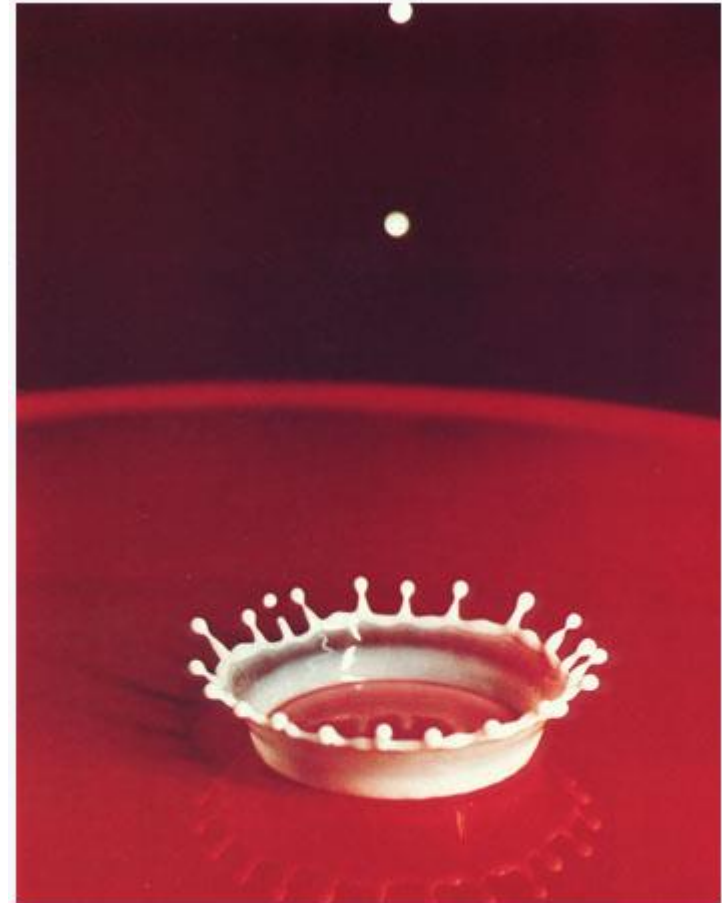
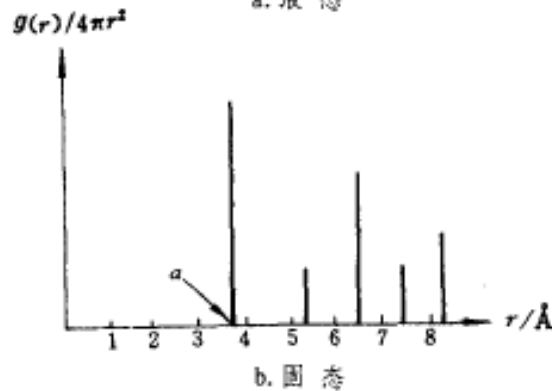
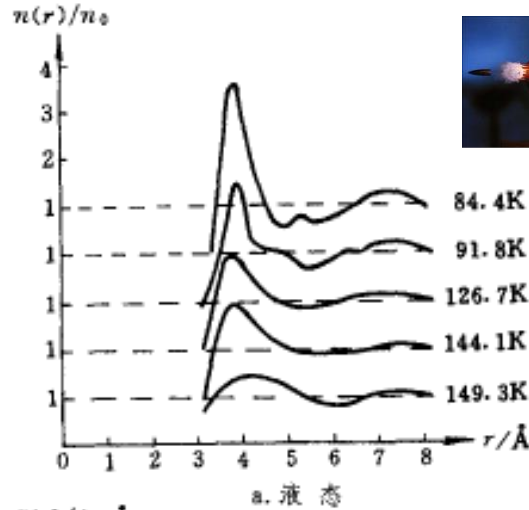
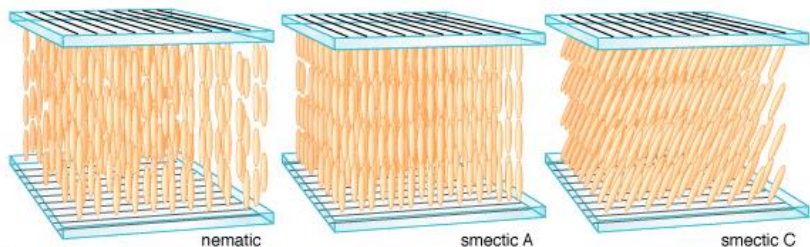
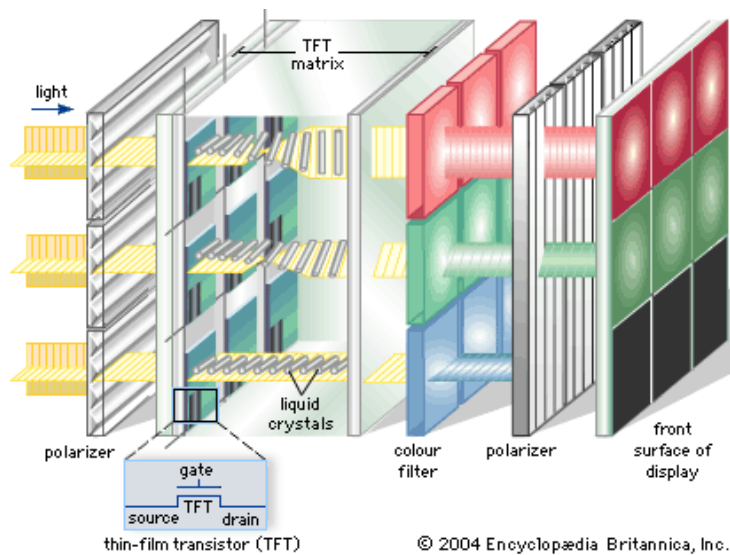
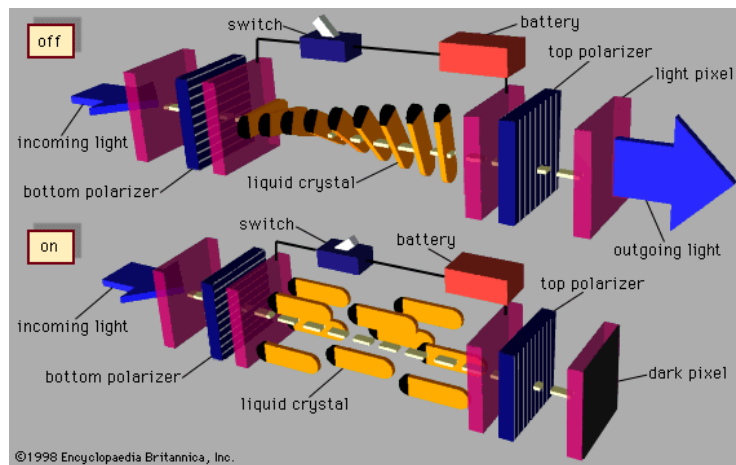


图 1-56 氩的径向分布函数

物质的气态、固态、液态



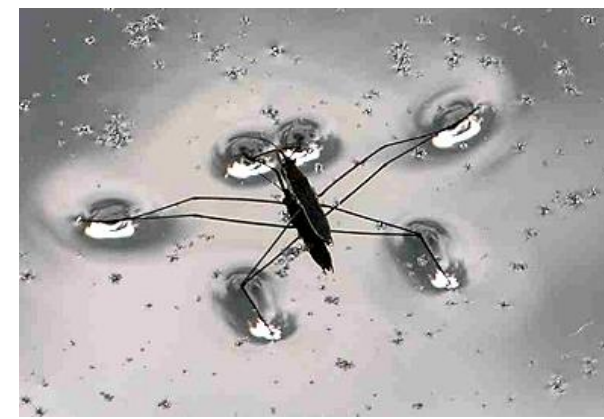
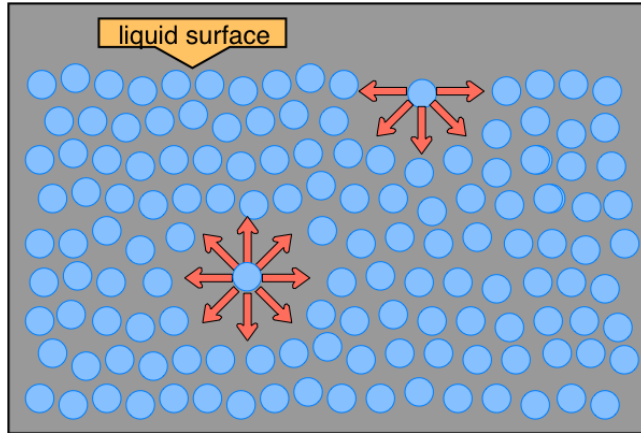
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液晶，包科达，《热物理学基础》，P240-242

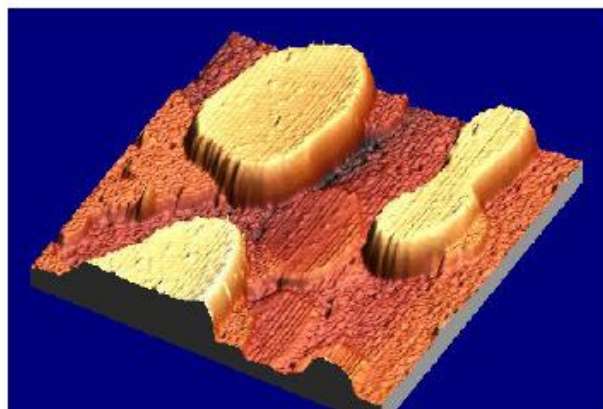
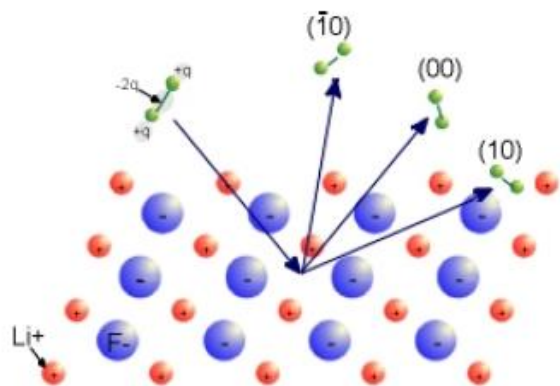
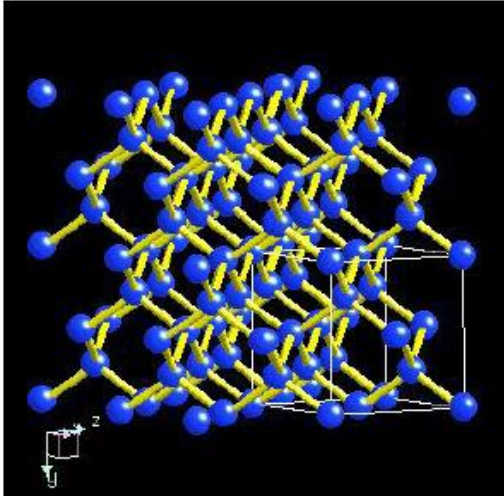
<http://dept.kent.edu/spie/liquidcrystals/>

表面张力

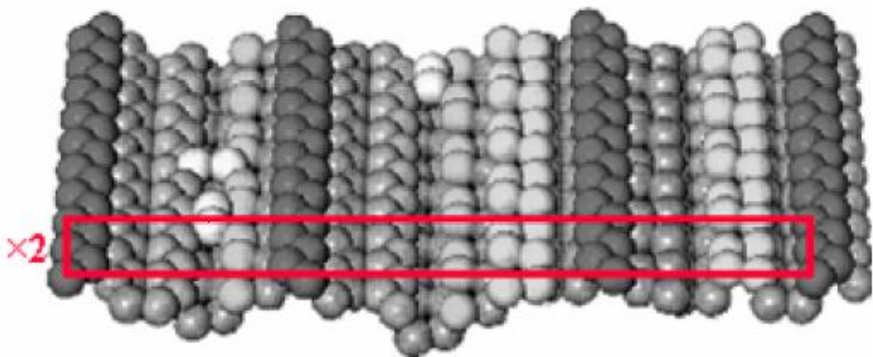


Surface Science is concerned with:

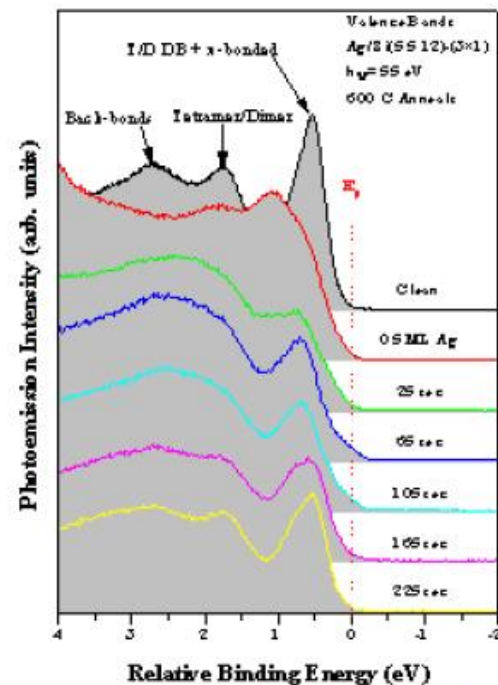
- Geometric structure
- Particle-Surface Interactions



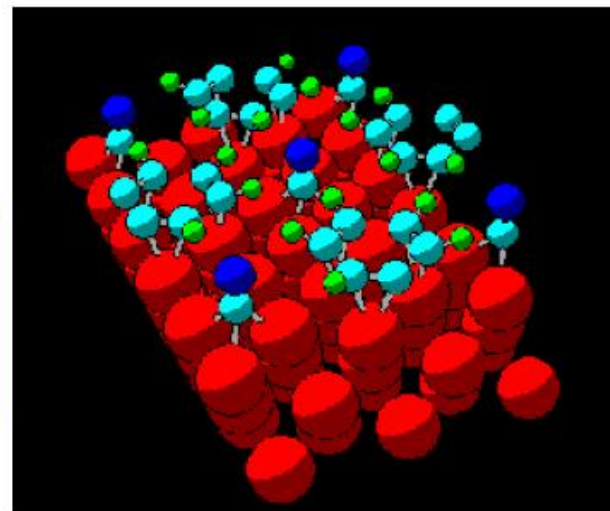
- Effects of radiation damage



- Chemical surface reactions



- Electronic structure



理想气体微观初级理论

作业

- 2.14, 2.20

大量事件的概率描述

例题：“热学”成绩

连续型描述

个人成绩：枚举

97,96,93,93,93,90,90,90,
90,88,88,87,87,87,86,86,
86,86,86,85,85,85,85,85,
85,83,83,82,82,82,82,82,
82,82,82,80,80,80,80,79,
79,79,79,79,79,79,78,78,
78,78,76,76,76,76,75,75,
75,75,75,75,75,75,73,
73,72,72,72,72,72,70,70,
69,68,68,66,65,64,64

随机变量 $x \in \mathbb{R}$ 且 $60 < x < 100$

概率 $P(x \rightarrow x + dx) = f(x)dx$

概率密度、分布 $f(x)$

归一化 $\int f(x)dx = 1$

平均值 $\bar{x} = \int xf(x)dx$

方差 $\sigma = \int (x - \bar{x})^2 f(x)dx$

离散型描述

随机变量 $x \in \{60, 61, \dots, 100\}$

概率 $P(x) = \frac{n(x)}{N} = \frac{n(x)}{\sum_x n(x)}$

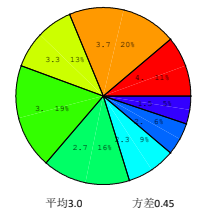
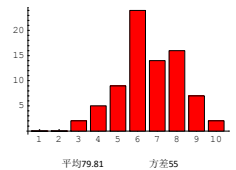
归一化 $\sum P(x) = 1$

平均值 $\bar{x} = \frac{\sum xn(x)}{\sum n(x)} = \sum x \frac{n(x)}{N}$

方差 $\sigma = \frac{\sum (x - \bar{x})^2 n(x)}{\sum n(x)} = \overline{x^2} - \bar{x}^2$

$$P(x \rightarrow x + dx, y \rightarrow y + dy, z \rightarrow z + dz) = f(x, y, z) dx dy dz$$

$$P(x \rightarrow x + dx, y \rightarrow y + dy, z \rightarrow z + dz) = f_x(x) f_y(y) f_z(z) dx dy dz$$



理想气体的微观模型

理想气体微观模型

- 1, 分子有质量、无体积, 是质点;
- 2, 除了相互碰撞的瞬间、以及和容器壁碰撞的瞬间之外分子不再受到其他作用。

微观描述

坐标 \mathbf{r}

速度 \mathbf{v}

动量 \mathbf{p}

能量 E

...

宏观描述

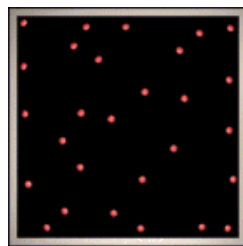
体积

压强

温度

内能

...



混乱, 数量多



统计描述

随机变量可选 \mathbf{r} 、 \mathbf{v} 、 \mathbf{p} 、 E 等

确定相应分布 $f(\mathbf{r})$ 、 $f(\mathbf{v})$ 、 $f(\mathbf{p})$ 、 $f(E)$ 等

求各种平均值

压强的统计解释

$$\vec{v} \rightarrow \vec{v} + d\vec{v}, \frac{N}{V} f(\vec{v}) dv_x dv_y dv_z$$

一个分子撞击器壁的后果,动量改变为 $2mv_x$

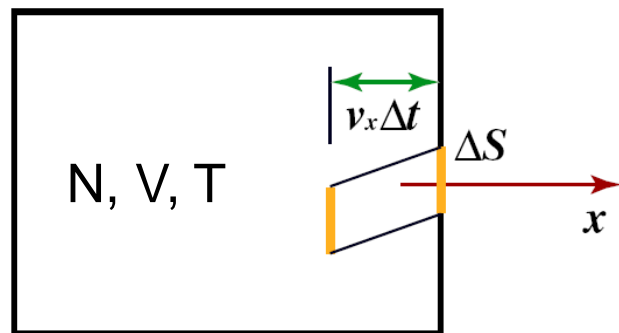
在时间 Δt 内, 速度为 \mathbf{v} 的分子沿着 \mathbf{v} 的方向走了 $\mathbf{v}\Delta t$, 沿 x 方向走了 $v_x\Delta t$, 而在以 ΔS 为底面积, $\mathbf{v}\Delta t$ 为母线长, $v_x\Delta t$ 为高的圆柱体内的所有速度为 \mathbf{v} , $v_x > 0$ 的分子都会撞到 ΔS 上

$$\Delta S v_x \Delta t \frac{N}{V} f(\vec{v}) dv_x dv_y dv_z \Big|_{v_x > 0}$$

$$\frac{1}{2} \Delta S v_x \Delta t \frac{N}{V} f(\vec{v}) dv_x dv_y dv_z$$

$$dp = \frac{2mv_x \frac{1}{2} \Delta S v_x \Delta t \frac{N}{V} f(\vec{v}) dv_x dv_y dv_z}{\Delta t \Delta S}$$

$$= mv_x^2 \frac{N}{V} f(\vec{v}) dv_x dv_y dv_z$$



P_x

$P_x v_x$

$\overline{P_x v_x}$

$$p = \iiint mv_x^2 \frac{N}{V} f(\vec{v}) dv_x dv_y dv_z = 2 \frac{N}{V} \frac{1}{2} \overline{mv_x^2}$$

$$\frac{1}{2} \overline{mv^2} = \frac{1}{2} m (\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}) = 3 \frac{1}{2} \overline{mv_x^2}$$

$$p = \frac{2}{3} \frac{N}{V} \frac{1}{2} \overline{mv^2} = \frac{1}{3} \frac{N}{V} \overline{\vec{p} \cdot \vec{v}}$$

宏观量

冲量作用的
统计平均

微观量

温度的统计解释

微观推导
状态方程

$$p = \frac{2}{3} \frac{N}{V} \overline{\frac{1}{2} m v^2}$$

$$p = \frac{N}{V} k_B T$$

宏观状
态方程

动能统
计平均

热动说

微观量

宏观量



$$\overline{\frac{1}{2} m v^2} = \frac{3}{2} k_B T$$



$$\overline{\frac{1}{2} m v_x^2} = \frac{1}{2} k_B T$$

$$\overline{\frac{1}{2} m v_y^2} = \frac{1}{2} k_B T$$

$$\overline{\frac{1}{2} m v_z^2} = \frac{1}{2} k_B T$$

能均分

$$\overline{\frac{1}{2} m v_x^2} = \frac{1}{3} \overline{\frac{1}{2} m v^2}$$

道尔顿分压定律

设一个容器体积为 V ，总压强为 p ，温度为 T ，总粒子数为 N ，质量为 M 。容器中盛有 n 种不同种类的气体，对于其中的任一种气体，其体积为 V ，压强为 p_i ，温度为 T ，粒子数为 N_i ，质量为 M_i 。

道尔顿
分压定律

$$p = \sum_{i=1}^n p_i$$

$$p_i = \frac{N_i}{V} k_B T$$

第 i 种理想气体
状态方程

$$p = \sum_{i=1}^n p_i = \sum_{i=1}^n \frac{N_i}{V} k_B T = \frac{\sum_{i=1}^n N_i}{V} k_B T = \frac{N}{V} k_B T$$

混合理想气体的状态方程

范氏气体状态方程修正参数的微观解释

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

$$\Delta p = \frac{\partial \Phi_N}{\partial V_0} = \frac{a}{V_0^2}$$

$$\Phi_N = \frac{1}{2} N_A (N_A - 1) \bar{\varphi}$$

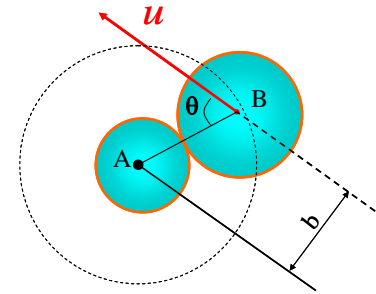
$$\bar{\varphi} = \int_d^\infty \varphi(r) \frac{4\pi r^2 dr}{V_0} = -\frac{\varepsilon}{V_0} \left(\frac{4}{3}\pi d^3\right)$$

$$r \leq d, \varphi(r) = \infty, r > d, \varphi(r) = -\varepsilon(d/r)^6$$

$$a = 4\varepsilon N_A^2 \frac{4}{3}\pi \left(\frac{d}{2}\right)^3$$

$$\text{He}, \varepsilon = 1.81 \times 10^{-22} \text{J},$$

$$a = 2.42 \times 10^{-2} \text{Jm}^3/\text{mol}^2$$



$$b = (N_A - 1) \times \frac{1}{2} \times \frac{4}{3}\pi d^3$$

$$\approx 4N_A \frac{4}{3}\pi \left(\frac{d}{2}\right)^3 \approx 0.01 \text{L/mol}$$

	氧	氮	氢	氦	氩	CO ₂	氨	H ₂ O
$a/(\text{atm} \cdot \text{L}^2/\text{mol}^2)$	1.36	1.35	0.245	0.032	1.35	3.60	4.19	5.48
$b/(10^{-2} \text{L/mol})$	3.19	3.86	2.66	2.34	3.23	4.28	3.73	3.06

麦克斯韦速度分布律

作业

- 3.19, 3.25

Maxwell-Boltzmann Distribution Law

微观描述

宏观描述

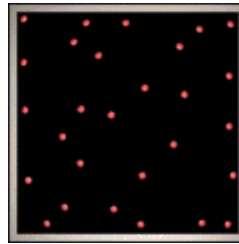
坐标 \mathbf{r}

速度 \mathbf{v}

动量 \mathbf{p}

能量 ε

...



体积

压强

温度

内能

...

统计描述

$$\frac{1}{3} \overline{\vec{p} \cdot \vec{v}} = p$$

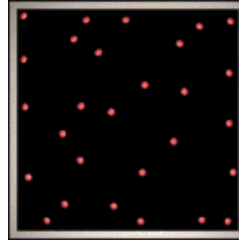
$$\frac{1}{2} \overline{mv^2} = \frac{3}{2} k_B T$$

$$N \overline{\varepsilon} = U$$

动量分布、速度分布、能量分布

Maxwell-Boltzmann Distribution Law

1859, Maxwell 提出
速度、速率分布律



1871, Boltzmann 推
广成能量分布律



概率描述,
各方向等价

$$v_i \rightarrow v_i + dv_i, f(v_i)dv_i$$

各方向独立

$$\vec{v} \rightarrow \vec{v} + d\vec{v}, f(v_x)f(v_y)f(v_z)dv_xdv_ydv_z$$

各向同性

$$f(v_x)f(v_y)f(v_z) = \phi(v_x^2 + v_y^2 + v_z^2)$$

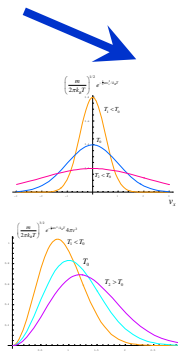
试探解 $f(v_x) = Ce^{-Av_x^2}, \phi(v_x^2 + v_y^2 + v_z^2) = C^3 e^{-A(v_x^2 + v_y^2 + v_z^2)}$

归一化 $1 = \iiint C^3 e^{-A(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \Rightarrow C = \sqrt{A/\pi}$

平均动能 $\iiint (A/\pi)^{3/2} \frac{1}{2} mv^2 e^{-Av^2} dv_x dv_y dv_z = \frac{3}{2} k_B T \Rightarrow A = m/2k_B T$

速度分布律
$$\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T} dv_x dv_y dv_z$$

速率分布律
$$\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T} 4\pi v^2 dv$$



例题:等温大
气密度分布

$$n(z) = n_0 e^{-mgz/k_B T}$$



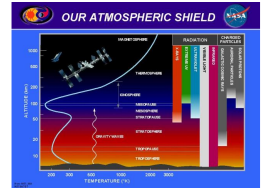
$$n(\vec{r}) = n_0 e^{-U(\vec{r})/k_B T}$$



Maxwell-Boltzmann Distribution Law

$$C' \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\varepsilon/k_B T} dv_x dv_y dv_z dx dy dz$$

ε is total molecular energy



密度分布律

例题 平均速度、方均根速率、速率、最概然速率

服从麦克斯韦速度分布律的气体分子质量为 m ，温度为 T ，求平均速

度 $\overline{v_x}$ $\overline{v_y}$ $\overline{v_z}$ 、方均根速率 $\sqrt{\overline{v^2}}$ 、平均速率 \overline{v} 、最概然速率 v_p 。

$$\overline{v_x} = \int_{-\infty}^{\infty} v_x g(v_x) dx = \int_{-\infty}^{\infty} \left(\frac{m}{2\pi k_B T}\right)^{1/2} v_x e^{-\frac{1}{2}mv_x^2/k_B T} dx = 0, \quad \overline{v_y} = \overline{v_z} = 0$$

$$\sqrt{\overline{v^2}} = \sqrt{\int_0^{\infty} v^2 F(v) dv} = \sqrt{\int_0^{\infty} v^2 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T} dv} = \sqrt{\frac{3k_B T}{m}}$$

$$\overline{v} = \int_0^{\infty} v F(v) dv = \int_0^{\infty} v 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T} dv = \sqrt{\frac{8k_B T}{\pi m}}$$

$$\left(4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T}\right)' \Big|_{v_p} = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left(2ve^{-\frac{1}{2}mv^2/k_B T} - \frac{mv^3}{k_B T} e^{-\frac{1}{2}mv^2/k_B T}\right) \Big|_{v_p} = 0 \Rightarrow v_p = \sqrt{\frac{2k_B T}{m}}$$

例题 星体周围大气的稳定性

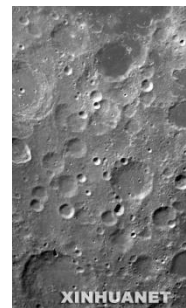


束缚与逃逸

$$v_{es} = \sqrt{\frac{2GM_e}{R_e}}, \quad v_p = \sqrt{\frac{2k_B T}{m}}$$

逃逸能力

$$K = \frac{v_{es}}{v_p} = \sqrt{\frac{2GM_e m}{2R_e k_B T}} \propto \sqrt{\frac{m}{T}}$$



$$\begin{aligned} M_m &= 0.012M_e \\ R_m &= 0.272R_e \\ K_m &= 0.2K_e \end{aligned}$$

气体	H ₂	He	CH ₄	H ₂ O	N ₂	O ₂	Ar	CO ₂
摩尔质量	2	4	16	18	28	32	40	44
K	7.2	10.2	20.4	21.6	26.9	28.8	32.2	33.8
百分比					78.08	20.95	0.93	0.03

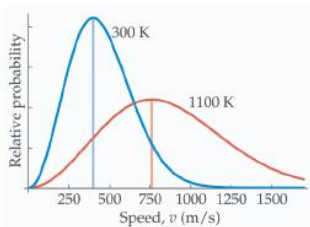
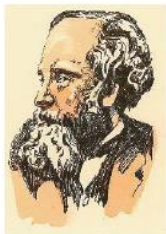
例题 分子按平动能的分布

根据麦克斯韦速率分布律求出分子平动能在 $\varepsilon \rightarrow \varepsilon + d\varepsilon$ 之间的概率

$$\begin{aligned} F(v)dv &= 4\pi v^2 \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T} dv \\ &= 4\pi \frac{2\varepsilon}{m} \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\varepsilon/k_B T} d\sqrt{\frac{2\varepsilon}{m}} \\ &= \frac{2}{\sqrt{\pi}} \left(\frac{1}{k_B T} \right)^{3/2} \varepsilon^{1/2} e^{-\varepsilon/k_B T} d\varepsilon \end{aligned}$$

$$f(\varepsilon)d\varepsilon = \frac{2}{\sqrt{\pi}} (k_B T)^{-3/2} \exp\left(-\frac{\varepsilon}{k_B T}\right) \sqrt{\varepsilon} d\varepsilon$$

速率分布律的实验验证

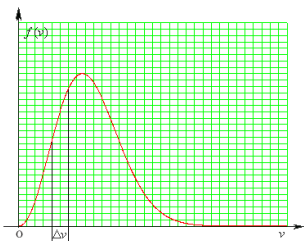


伟大的英国物理学家麦克斯韦 (J.C. Maxwell, 1831-1879) 以及他提出的关于气体分子的速率分布。

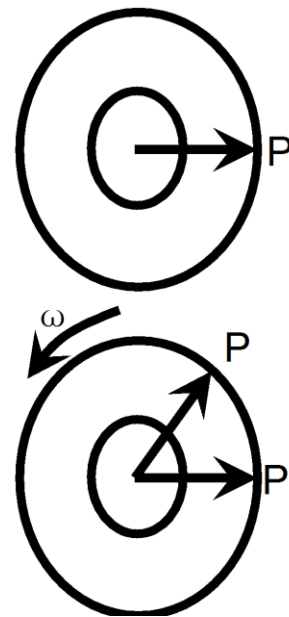
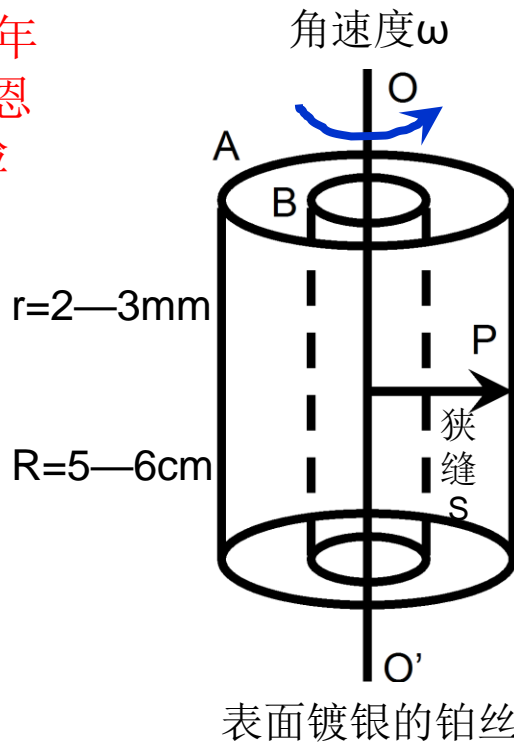
$$\left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T} 4\pi v^2 dv$$



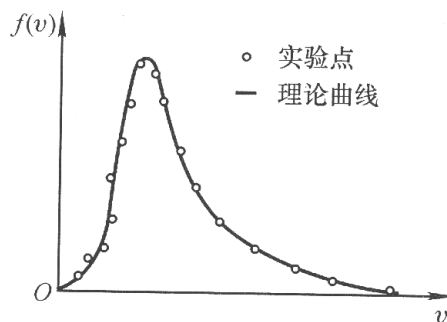
Maxwell速率分布为最概然分布的模拟



1920年
斯特恩
实验



银分子
厚度正
比于分
子数



$$l = R\omega\Delta t = R\omega \frac{R-r}{v}$$

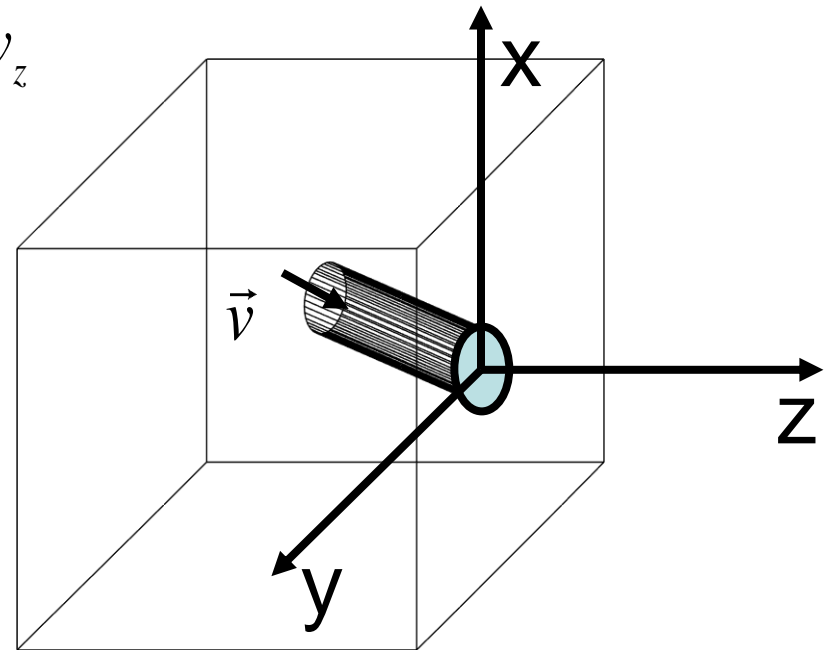
$$\Rightarrow v = \frac{R(R-r)\omega}{l}$$

例题

泻流。容器中充满某种气体，放于真空中，器壁上有一个小孔，这样分子会从小孔逃逸，这被称为泻流现象。假设泻流出去的分子不改变容器中气体的平衡态分布，并且泻流出去的分子相互之间没有碰撞，求出泻流出去的气体分子的速度分布与速率分布，并计算泻流分子的平均动能、平均速度、平均速率、最概然速率。

$$v_x \rightarrow v_x + dv_x, v_y \rightarrow v_y + dv_y, v_z \rightarrow v_z + dv_z$$

$$\begin{aligned} \frac{d\Gamma}{\Gamma} &= \frac{\frac{N}{V} v_z f(\vec{v}) dv_x dv_y dv_z}{\frac{1}{4} \frac{N}{V} \bar{v}} \\ &= \frac{4v_z f(\vec{v}) dv_x dv_y dv_z}{\bar{v}} \end{aligned}$$



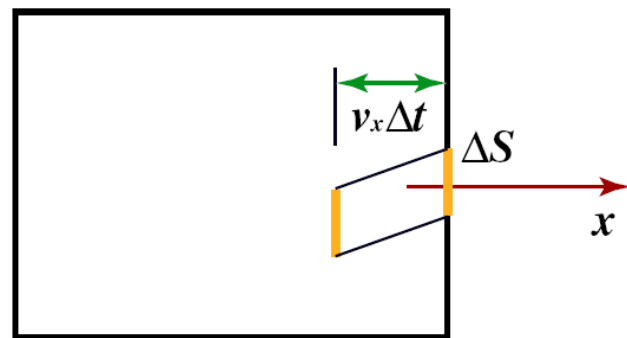
例题

气体分子碰壁数。容器中充满某种气体，求单位时间内，碰撞到容器壁上单位面积上的气体分子数目。

$$v_x \rightarrow v_x + dv_x, v_y \rightarrow v_y + dv_y, v_z \rightarrow v_z + dv_z$$

$$\frac{N}{V} f(\vec{v}) dv_x dv_y dv_z$$

$$\Delta S v_x \Delta t \frac{N}{V} f(\vec{v}) dv_x dv_y dv_z \Big|_{v_x > 0}$$



$$d\Gamma = \frac{\Delta S v_x \Delta t \frac{N}{V} f(\vec{v}) dv_x dv_y dv_z}{\Delta S \Delta t} = \frac{N}{V} v_x f(\vec{v}) dv_x dv_y dv_z$$

$$\Gamma = \int d\Gamma = \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z \int_0^{\infty} \frac{N}{V} v_x f(\vec{v}) dv_x = \frac{1}{4} \frac{N}{V} \bar{v}$$

例题 泻流分离同位素

分子质量分别为 m_1, m_2 的两种气体相混合，温度为 T ，分子数密度为 n_1, n_2 ，则发生泻流之后的气体中两种气体的分子数目之比为

$$\frac{I_1}{I_2} = \frac{\Gamma_1}{\Gamma_2} = \frac{n_1 \bar{v}_1}{n_2 \bar{v}_2} = \frac{n_1}{n_2} \left(\frac{m_2}{m_1} \right)^{1/2}$$

质量之比为

$$\frac{I_1 m_1}{I_2 m_2} = \frac{n_1}{n_2} \left(\frac{m_1}{m_2} \right)^{1/2}$$

同位素分离

$$\frac{I_1}{I_2} = \frac{n_1}{n_2} \left[\left(\frac{m_2}{m_1} \right)^{1/2} \right]^n \Rightarrow n = \frac{\ln \frac{I_1 / I_2}{n_1 / n_2}}{\ln \left(\frac{m_2}{m_1} \right)^{1/2}}$$



U^{235} 可裂变

0.72% \rightarrow 0.99

$n=2232$

麦玻分布与能均分定理

作业

- 3.24, 3.30

Maxwell-Boltzmann Distribution Law

微观描述

宏观描述

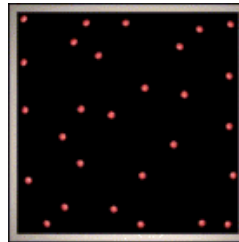
坐标 \mathbf{r}

速度 \mathbf{v}

动量 \mathbf{p}

能量 ε

...



体积

压强

温度

内能

...

↓
统计描述

$$\frac{1}{3} \overline{\vec{p} \cdot \vec{v}} = p$$

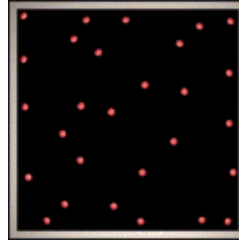
$$\frac{1}{2} \overline{mv^2} = \frac{3}{2} k_B T$$

$$N \overline{\varepsilon} = U$$

↑
动量分布、速度分布、能量分布

Maxwell-Boltzmann Distribution Law

1859, Maxwell 提出
速度、速率分布律



1871, Boltzmann 推
广成能量分布律



概率描述,
各方向等价

$$v_i \rightarrow v_i + dv_i, f(v_i)dv_i$$

各方向独立

$$\vec{v} \rightarrow \vec{v} + d\vec{v}, f(v_x)f(v_y)f(v_z)dv_xdv_ydv_z$$

各向同性

$$f(v_x)f(v_y)f(v_z) = \phi(v_x^2 + v_y^2 + v_z^2)$$

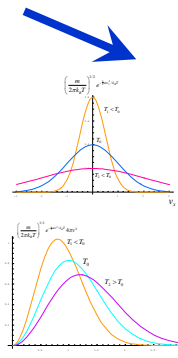
试探解 $f(v_x) = Ce^{-Av_x^2}, \phi(v_x^2 + v_y^2 + v_z^2) = C^3 e^{-A(v_x^2 + v_y^2 + v_z^2)}$

归一化 $1 = \iiint C^3 e^{-A(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \Rightarrow C = \sqrt{A/\pi}$

平均动能 $\iiint (A/\pi)^{3/2} \frac{1}{2} mv^2 e^{-Av^2} dv_x dv_y dv_z = \frac{3}{2} k_B T \Rightarrow A = m/2k_B T$

速度分布律
$$\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T} dv_x dv_y dv_z$$

速率分布律
$$\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T} 4\pi v^2 dv$$

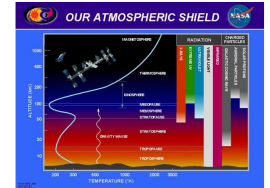


例题:等温大
气密度分布

$$n(z) = n_0 e^{-mgz/k_B T}$$



$$n(\vec{r}) = n_0 e^{-U(\vec{r})/k_B T}$$



密度分布律

Maxwell-Boltzmann Distribution Law

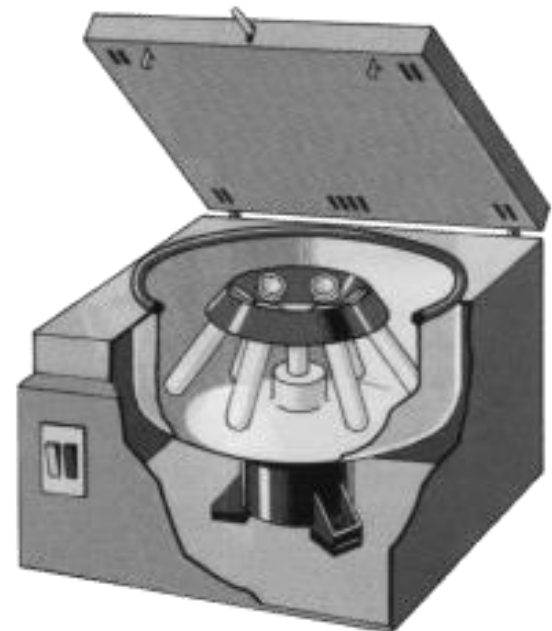
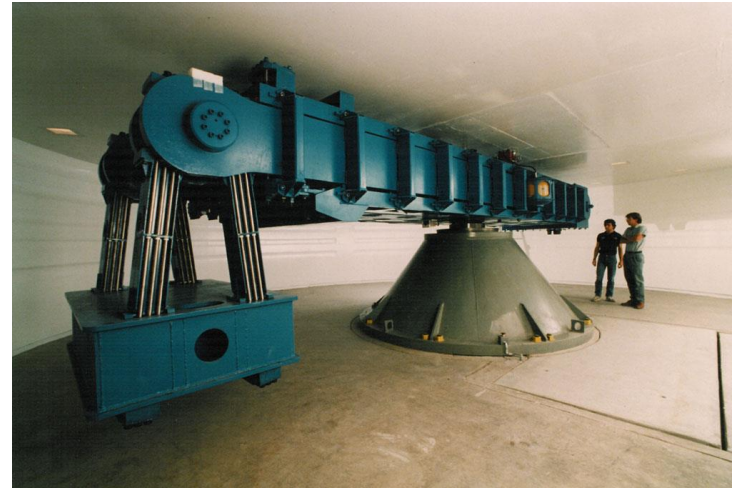
$$C' \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\varepsilon/k_B T} dv_x dv_y dv_z dx dy dz$$

ε is total molecular energy

例题 离心势能下密度分布律

$$U(r) = -\int_0^r m\omega^2 r dr = -\frac{1}{2} m\omega^2 r^2$$

$$n(r) = n_0 e^{\frac{1}{2} m\omega^2 r^2 / k_B T}$$



自由度

非刚性双原子分子



用坐标(x,y,z)确定质心位置，平动自由度为**3**

$$\frac{1}{2m}(p_{cx}^2 + p_{cy}^2 + p_{cz}^2)$$

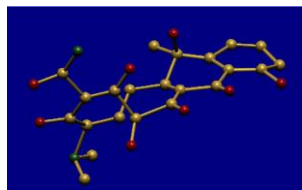
用球坐标系中的坐标确定两个原子连线的方位，即转动自由度为**2**

$$\frac{p_{\theta}^2}{2I_{\theta}} + \frac{p_{\phi}^2}{2I_{\phi}}$$

用球坐标系中的坐标r确定两个原子之间的相对距离，即振动自由度为**1**

$$\frac{p_s^2}{2m_r} + \frac{1}{2}m_r\omega^2q^2$$

共需要**6**个自由度



n原子分子

质心位置，平动自由度为**3**

用球坐标系中的坐标确定转轴和转角，自由度为**3**

原子间的振动自由度，共**3n-6**

共需要**3n**个自由度

能均分定理

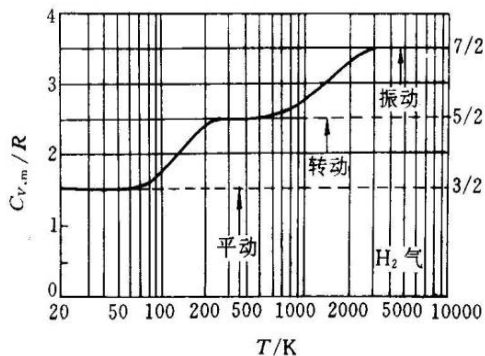
理想气体的
内能与热容

$$U = N\bar{\varepsilon} = (t+r+2s)\frac{1}{2}Nk_B T$$

$$= (t+r+2s)\frac{1}{2}nRT$$

$$c_V = (t+r+2s)\frac{1}{2}R$$

$$\text{H}_2 \quad c_V = \frac{7}{2}R$$



能均分定理：在热平衡状态下，物质（气体、液体、固体）分子的每一自由度都具有相同的平均动能，在温度 T 下其数值为 $k_B T/2$

$$\tilde{a}_i = g_i e^{-\alpha - \beta \varepsilon_i}$$

$$\varepsilon = \frac{1}{2} \sum_{i=1}^m a_i p_i^2 + \frac{1}{2} \sum_{j=1}^n b_j q_j^2 + E_p(q_{n+1}, q_{n+2}, \dots, q_r)$$

$$\overline{\text{平方项}} = \frac{1}{2} k_B T$$

开尔文勋爵：20世纪物理学上空的两朵乌云

热辐射

固体的
热容量

$$U = 3Nk_B T = 3nRT$$

$$c = 3R$$

Dulong-Petit Law
Blotzmann 导出

表 2-6 几种固体在室温下的摩尔热容量

物质	C^{mol}/R	物质	C^{mol}/R
铝 Al	3.09	铜 Cu	2.97
金刚石 C	0.68	锡 Sn	3.34
铁 Fe	3.18	铂 Pt	3.16
金 Au	3.20	银 Ag	3.09
镉 Cd	3.08	锌 Zn	3.07
硅 Si	2.36	硼 B	1.26

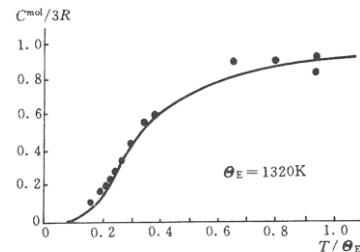


图 2-17 爱因斯坦理论曲线与金刚石热容量的拟合

微观粒子的量子力学描述

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \psi(\vec{r}, t)$$

态函数描述
粒子在空间的
概率分布

全同性：处于相
同态上的粒子是
不可分辨的

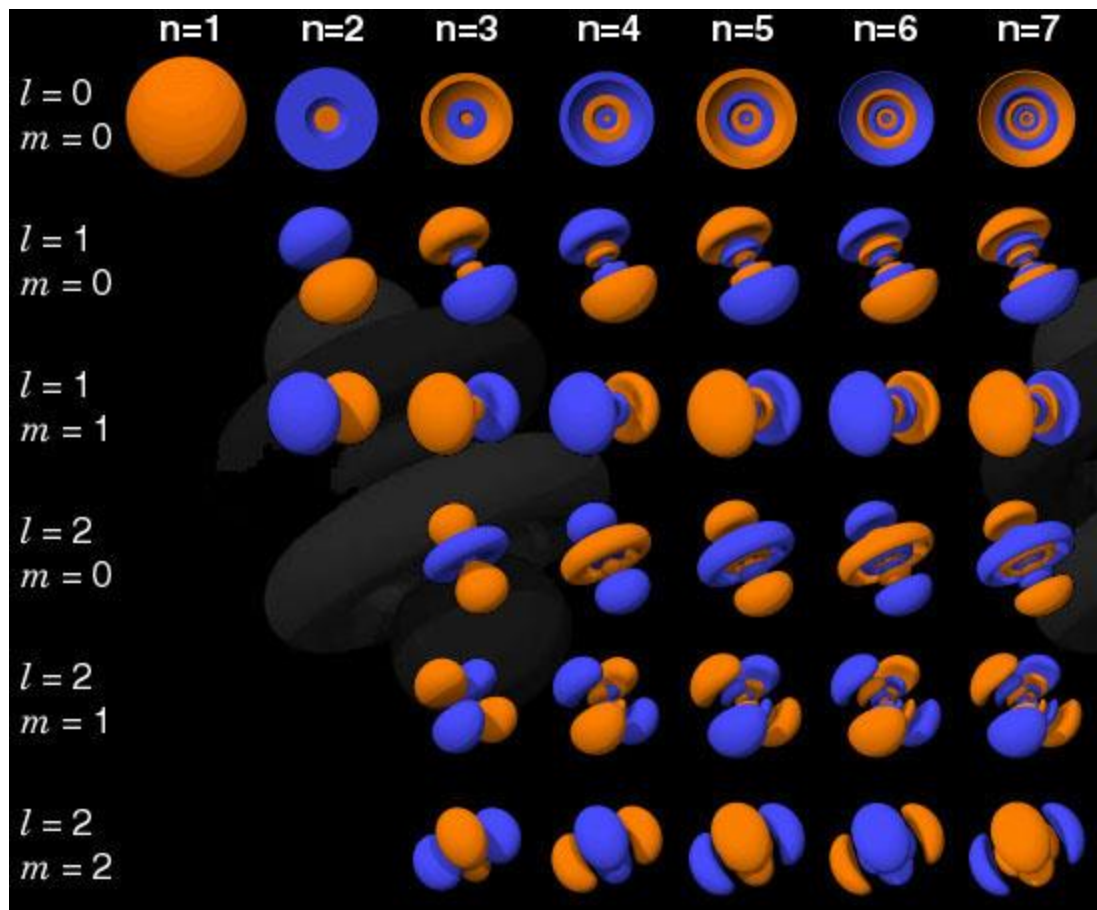
量子数标记不
同的态函数

能量：离散能级 ϵ_i
简并度 g ，当 $g > 1$
时，能级是简并的

自旋 S ：整数，玻色
子，不服从泡利不
相容原理。半奇数，
费米子，服从泡利
不相容原理。

轨道角动量
总角动量

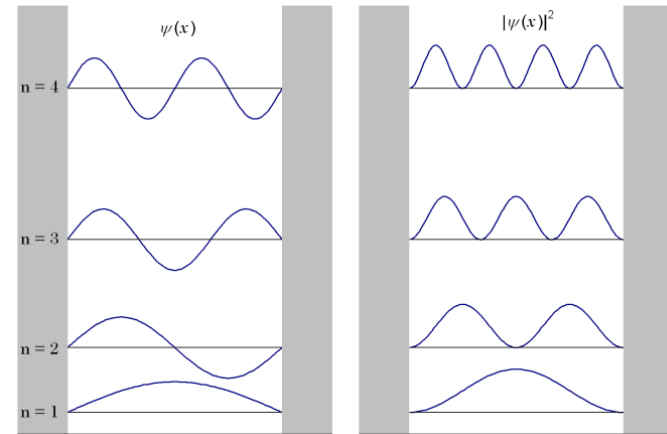
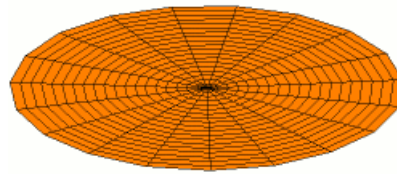
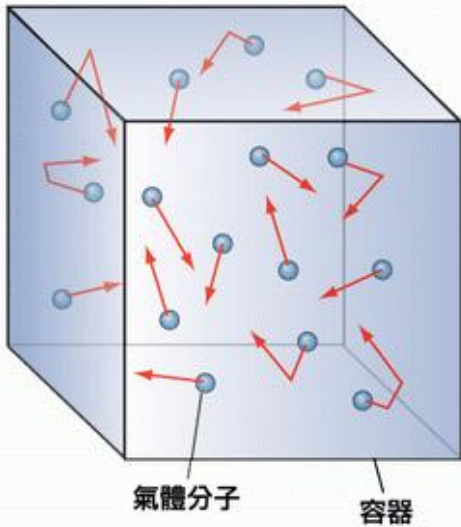
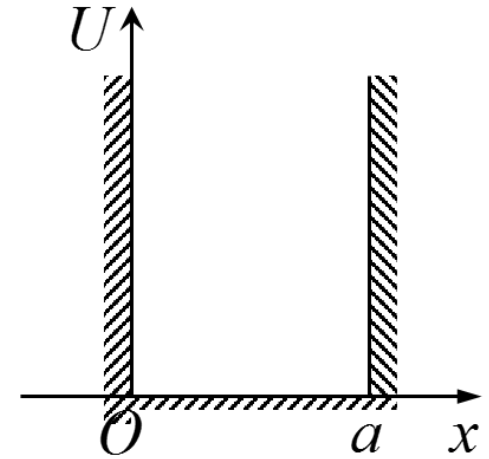
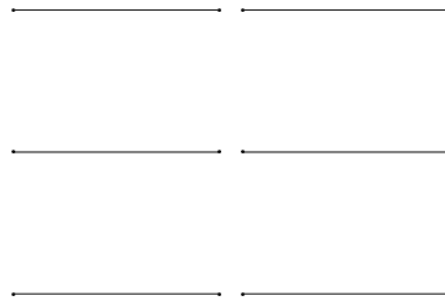
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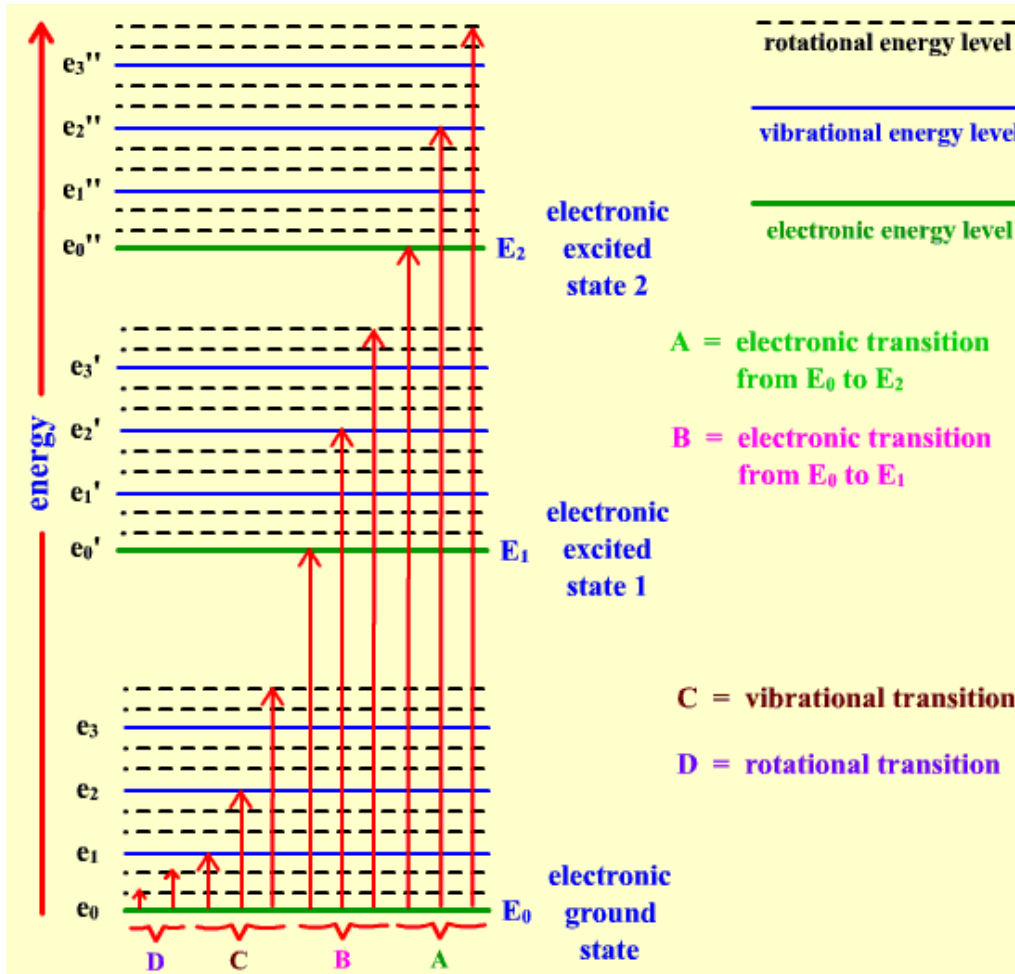
束缚在箱子中的气体分子

$$\Delta x \Delta p \geq \hbar/2$$

$$\lambda \sim h/p$$



多原子分子的能级与能谱



电子运动能量

$$E_e = \frac{p^2}{2m} \sim \frac{(\Delta p)^2}{2m} \sim \frac{\hbar^2}{2ma^2} \approx 4\text{eV}$$

分子振动能量

$$E_v = \hbar\omega = \hbar\sqrt{\frac{k}{\mu}}, \quad E_e = \frac{1}{2}ka^2$$

$$E_v \sim \sqrt{E_e ma^2} \sqrt{\frac{2E_e}{\mu a^2}} = \left(\frac{m}{\mu}\right)^{1/2} E_e$$

分子转动能量

$$E_r = \frac{p_\phi^2}{2I} \sim \frac{\hbar^2}{\mu a^2} \sim \frac{m}{\mu} E_e$$

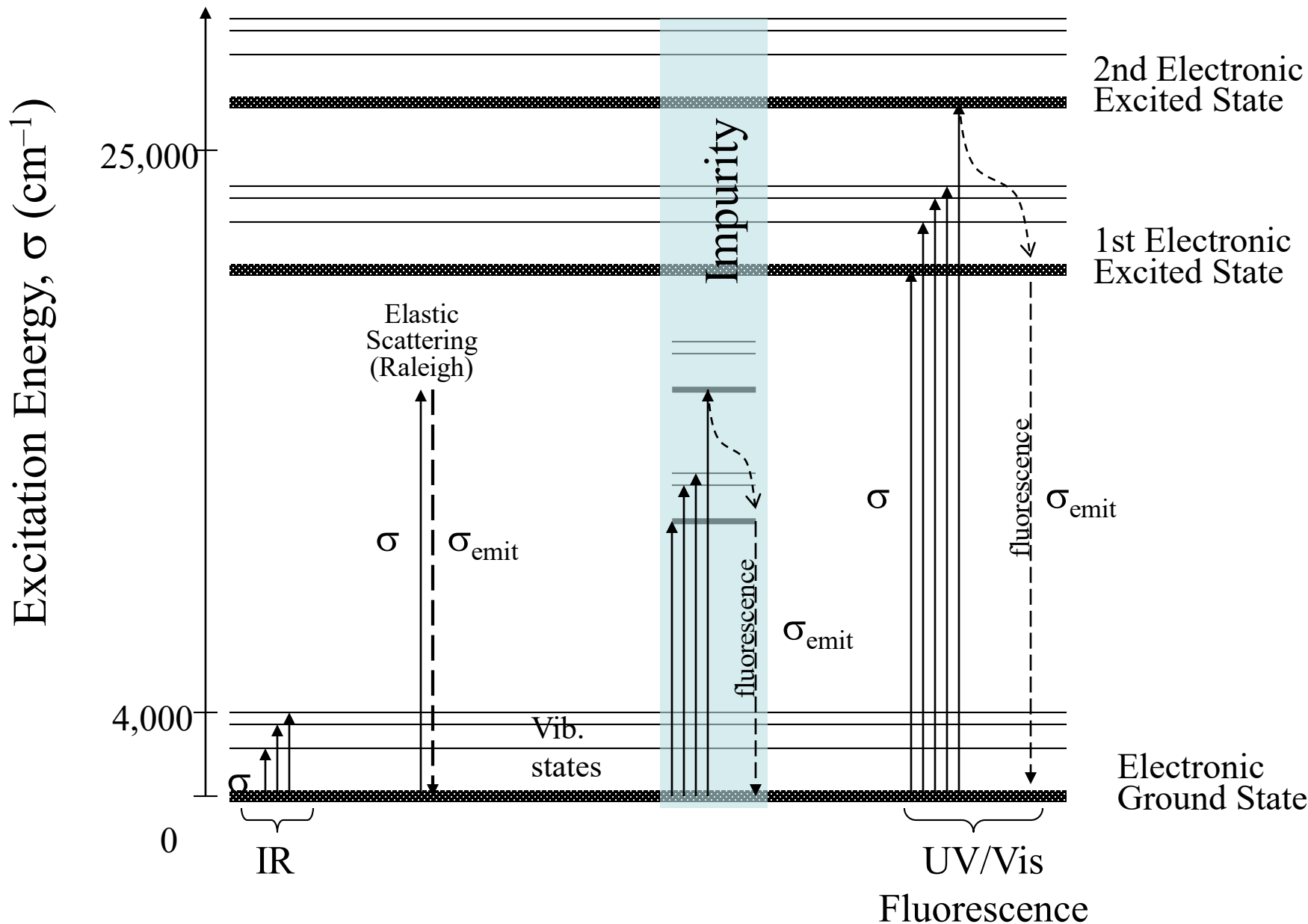
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电子运动与分子运动可独立考虑

Transition and Energy of Light

transition	rotational transition	vibrational transition	electronic transition	
			E_0 to E_1	E_0 to E_2
range of absorption	far-IR / MW	near- & mid-IR	near-UV /VIS	far-UV

Main Optical Transitions: Absorption, Scattering, and Fluorescence



理想气体热容、固体热容

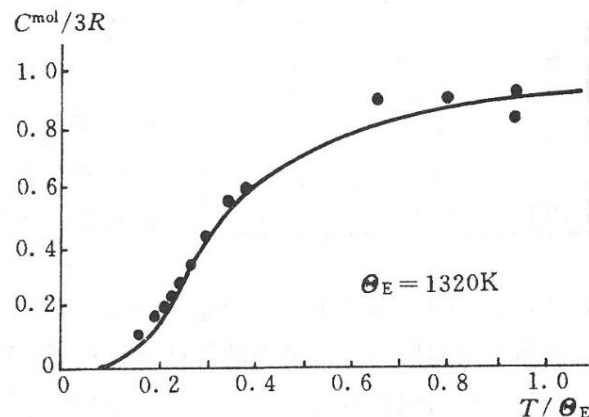
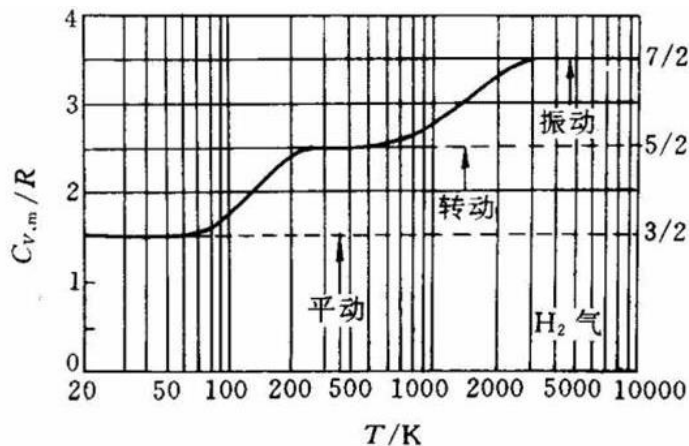


图 2-17 爱因斯坦理论
曲线与金刚石热容量的拟合

$$\varepsilon_l = \frac{l(l+1)}{2J} = l(l+1)k_B\theta_r, g_l = 2l+1$$

$$z = \sum_l g_l e^{-\varepsilon_l/k_B T} \approx 1 + 3e^{-2\theta_r/T}$$

$$\ln z \approx 3e^{-2\theta_r/T}$$

$$E = -N \frac{\partial \ln z}{\partial \beta} \approx 6Nk_B\theta_r e^{-2k_B\theta_r\beta}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \approx 12Nk_B \left(\frac{\theta_r}{T} \right)^2 e^{-2\theta_r/T}$$

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar\omega = \left(n + \frac{1}{2} \right) k_B\theta_V, g_n = 1$$

$$z = \sum_n g_n e^{-\varepsilon_n/k_B T} = \frac{e^{-\theta_V/2T}}{1 - e^{-\theta_V/T}}$$

$$\ln z = -\theta_V/2T - \ln(1 - e^{-\theta_V/T})$$

$$E = -3N \frac{\partial \ln z}{\partial \beta} = 3Nk_B\theta_V/2 + 3N \frac{k_B\theta_V}{e^{\beta k_B\theta_V} - 1}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3Nk_B \left(\frac{\theta_V}{T} \right)^2 \frac{e^{\theta_V/T}}{(e^{\theta_V/T} - 1)^2}$$

基于量子力学的麦玻分布

作业

- 6.30

例题 二项分布

理想气体体积为V，总粒子数为N，体积分为左右两半，处于左边的概率为p，右边的概率为q，两者之和为1

随机变量x，取左右两个值

微观态排列{ $n, N-n$ }
每种排列出现的概率为 $p^n q^{N-n}$

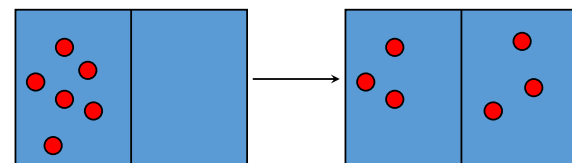
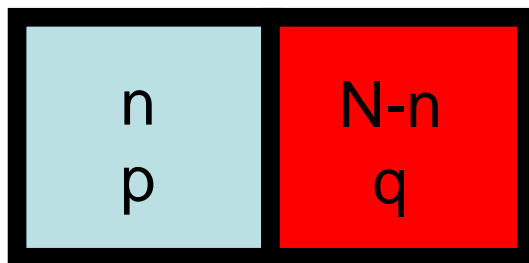
宏观态组合
{ $n, N-n$ }, $n \in [0, N]$,
出现的概率为

$$C_N^n p^n q^{N-n}$$

伯努利二项分布



涨落



熵增加

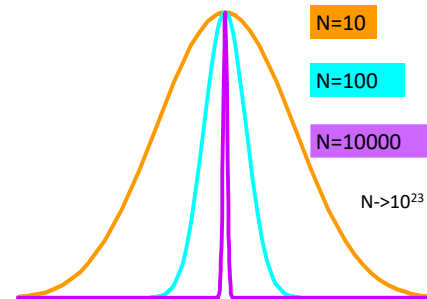
最概然分布、平衡态、平均分布

取 $p=q=1/2$, 则二项分布变为

$$C_N^n / 2^N$$

最概然分布为 $n \approx N/2$

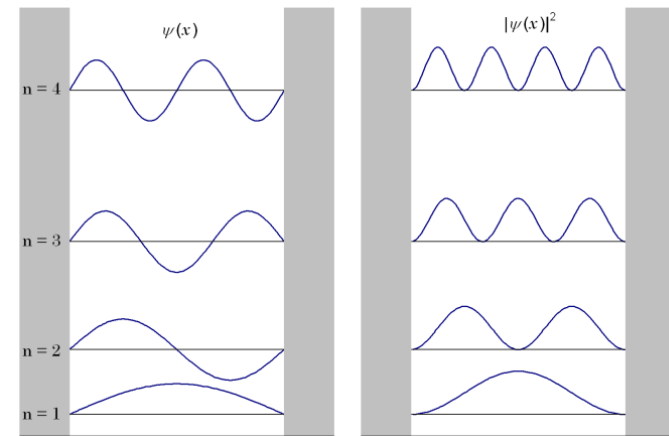
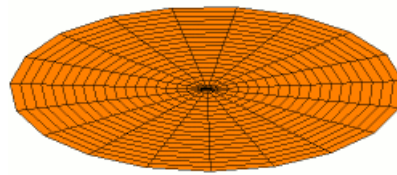
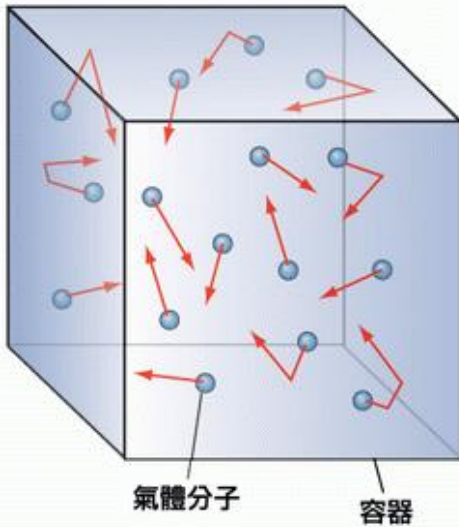
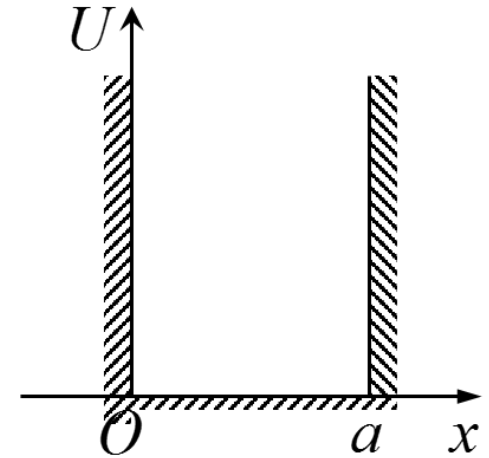
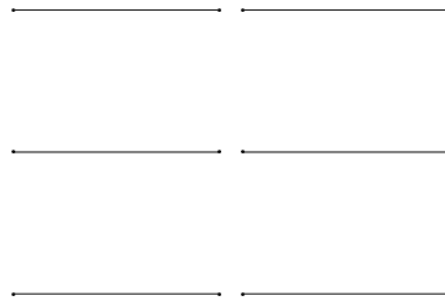
$$C_N^{N/2} / 2^N$$



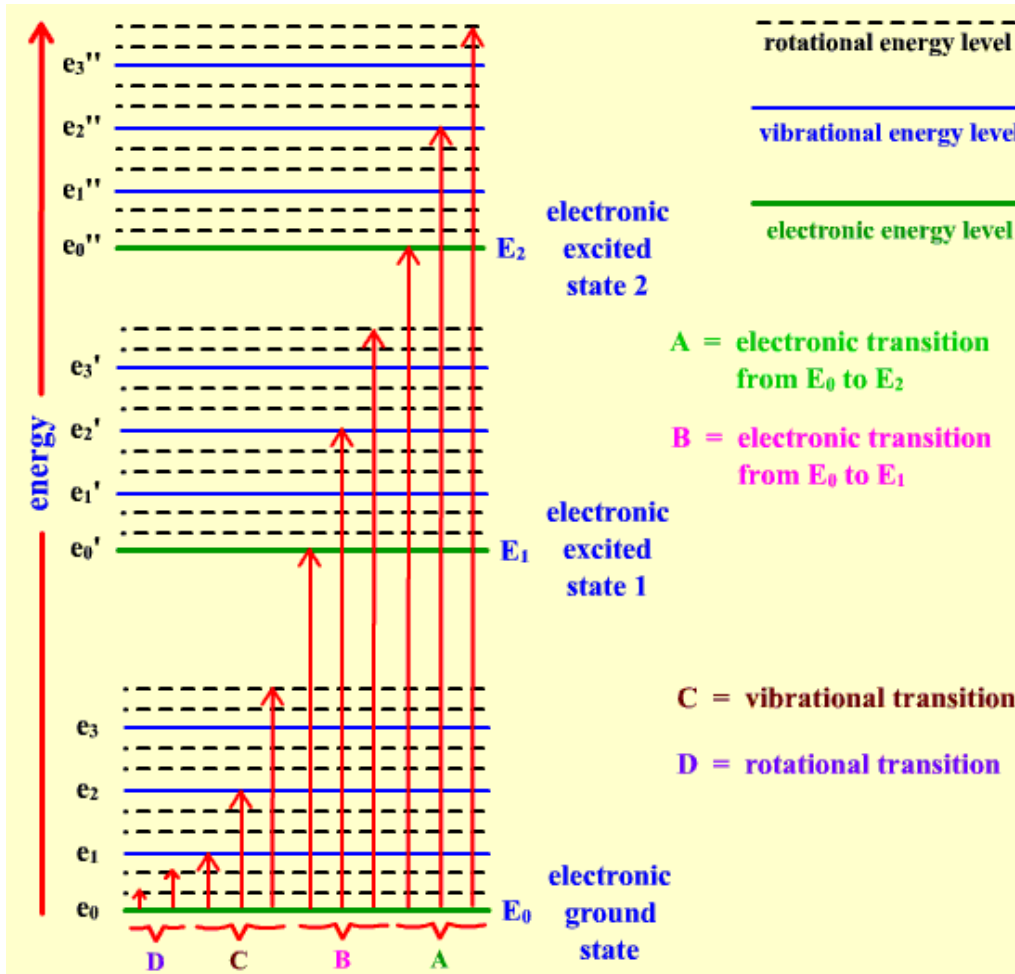
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$$E_r = \frac{p_\phi^2}{2I} \sim \frac{\hbar^2}{\mu a^2} \sim \frac{m}{\mu} E_e$$

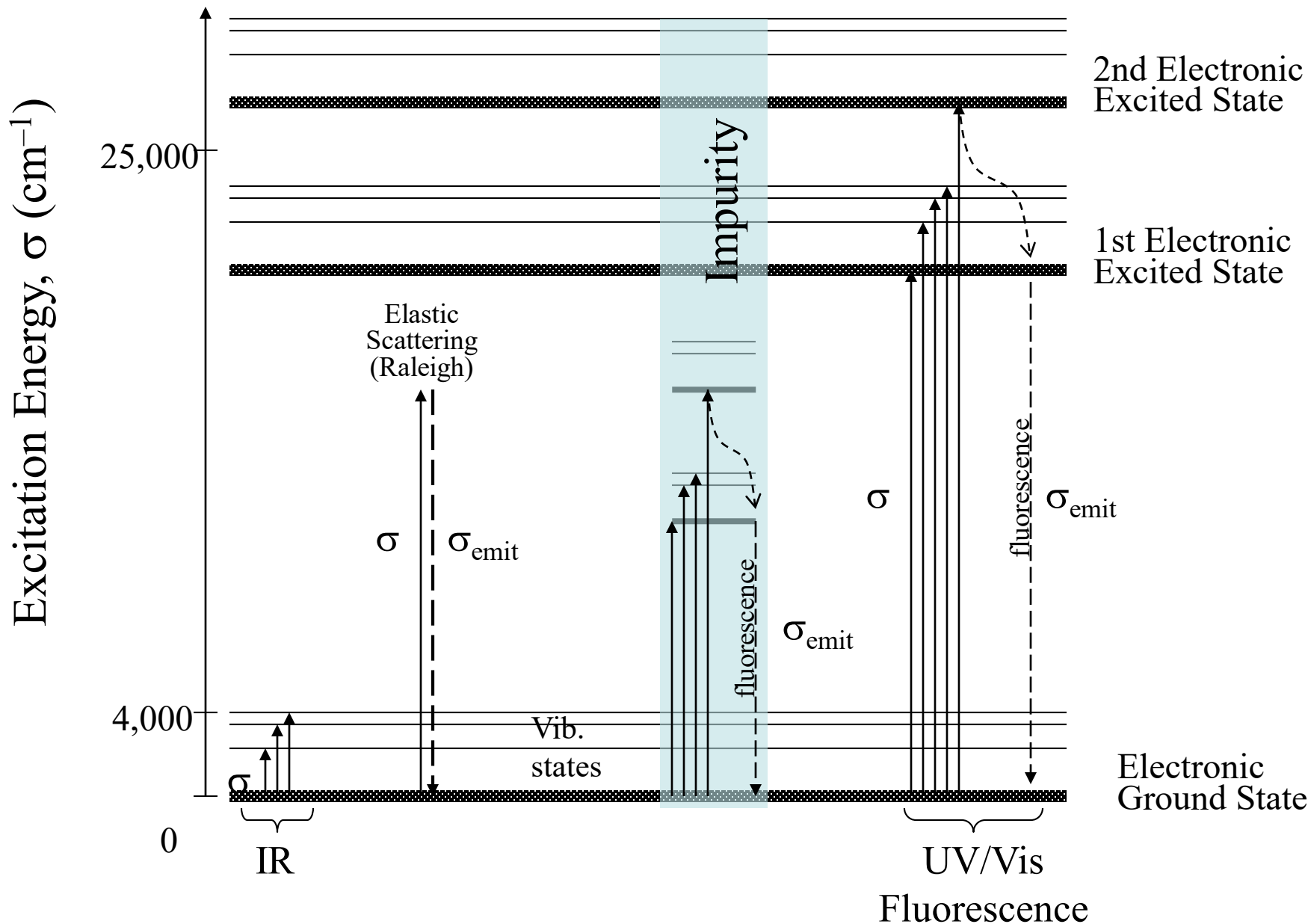
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Main Optical Transitions: Absorption, Scattering, and Fluorescence



Maxwell-Boltzmann Distribution Law

可分辨系统—定域子系

粒子按能级的分布

宏观分布对应的微观状态数

$$N, E, \{\varepsilon_i\}, \{g_i\}, \{a_i\}$$

粒子数守恒 $\left\{ \begin{array}{l} N = \sum_i a_i \\ E = \sum_i a_i \varepsilon_i \end{array} \right. \Rightarrow \left\{ \begin{array}{l} \sum_i \delta a_i = 0 \\ \sum_i \varepsilon_i \delta a_i = 0 \end{array} \right.$

能量守恒

近独立子系

各态历经

等概率假设

$$W = \frac{N!}{\prod_i a_i!} \prod_i g_i^{a_i} \Rightarrow \ln W = \ln N! + \sum_i a_i \ln g_i - \sum_i \ln a_i!$$

热力学概率
未归一化

$$S = k_B \ln W$$

Boltzmann熵



最可几分布

$$\delta \ln W = 0, \delta^2 \ln W < 0$$

拉格朗日乘子法

$$\delta \left(\ln W - \alpha \sum_i a_i - \beta \sum_i a_i \varepsilon_i \right) = 0$$

Sterling公式

$$\ln n! = \sum_{i=1, n} \ln i \approx \int_0^n \ln x dx = n \ln n - n$$

Maxwell-Boltzmann Distribution Law

$$\begin{aligned}\delta \ln W &= \sum_i \ln g_i \delta a_i - \sum_i \delta \ln a_i ! \\ &= \sum_i \ln g_i \delta a_i - \sum_i \ln a_i \delta a_i \\ &= - \sum_i \left(\ln \frac{a_i}{g_i} \right) \delta a_i\end{aligned}$$

$$- \sum_i \ln \frac{a_i}{g_i} \delta a_i - \alpha \sum_i \delta a_i - \beta \sum_i \varepsilon_i \delta a_i = 0$$

$$\sum_i \left(\ln \frac{a_i}{g_i} + \alpha + \beta \varepsilon_i \right) \delta a_i = 0$$

$$\ln \frac{a_i}{g_i} + \alpha + \beta \varepsilon_i = 0$$

Maxwell-Boltzmann Distribution Law

$$\delta^2 \ln W = -\sum_i \frac{(\delta \tilde{a}_i)^2}{\tilde{a}_i} < 0$$

$$g_i \propto d\vec{v}d\vec{r}$$

$$f(\vec{v}, \vec{r})d\vec{v}d\vec{r} = C e^{-\beta \varepsilon} d\vec{v}d\vec{r}$$

$$\ln \frac{W}{\tilde{W}} = -\sum_i \tilde{a}_i \frac{1}{2} \delta_i^2 = -N \overline{\frac{1}{2} \delta_i^2}$$

$$\tilde{a}_i = g_i e^{-\alpha - \beta \varepsilon_i}$$

MB分布

平均分布与最概然分布
平衡态与细致平衡原理
赵凯华,《新概念热学》,P91-93
熵增加原理

子系配分函数

$$Z = \sum_i g_i e^{-\beta \varepsilon_i}, e^{-\alpha} = N / Z$$

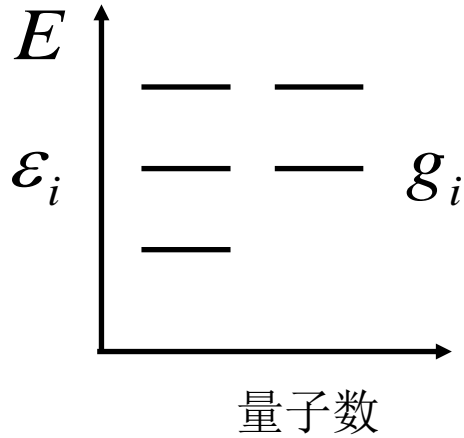
$$E = \frac{N}{Z} \sum_i g_i e^{-\beta \varepsilon_i} \varepsilon_i = -N \frac{\partial \ln Z}{\partial \beta}$$

$$\begin{cases} N = \sum_i \tilde{a}_i = \sum_i g_i e^{-\alpha - \beta \varepsilon_i} \\ E = \sum_i \tilde{a}_i \varepsilon_i = \sum_i g_i e^{-\alpha - \beta \varepsilon_i} \varepsilon_i \end{cases}$$

理想气体平均动能 $\rightarrow \beta = \frac{1}{k_B T}$

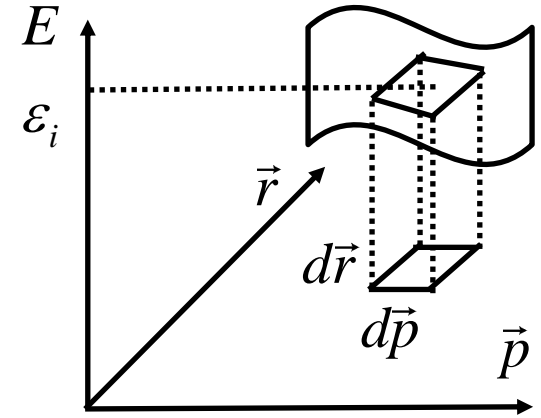
定域子系的经典极限条件

量子力学



$$g_i = \frac{dp_x dp_y dp_z dx dy dz}{h^3}$$

经典力学



经典极限条件



$$\Delta\varepsilon \ll k_B T$$

$$\tilde{a}_i = g_i e^{-\alpha - \beta\varepsilon_i}$$

$$f(\vec{v}, \vec{r}) d\vec{v} d\vec{r} = \frac{\tilde{a}_i}{N} = \frac{e^{-\alpha} m^3}{N h^3} e^{-\beta\varepsilon} d\vec{v} d\vec{r}$$

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

子系配分函数

$$Z = \int e^{-\beta\varepsilon} \frac{dp_1 \cdots dp_r dq_1 \cdots dq_r}{h^r}$$

理想气体热容、固体热容

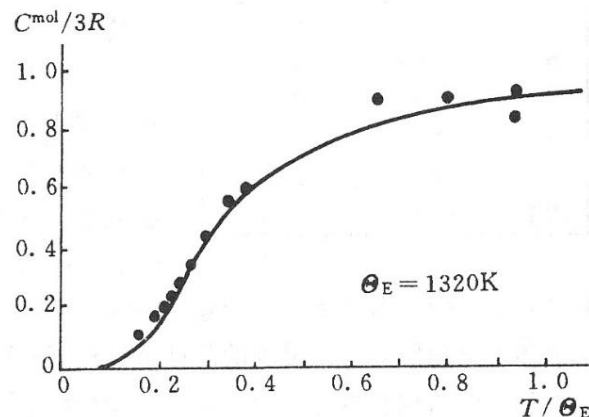
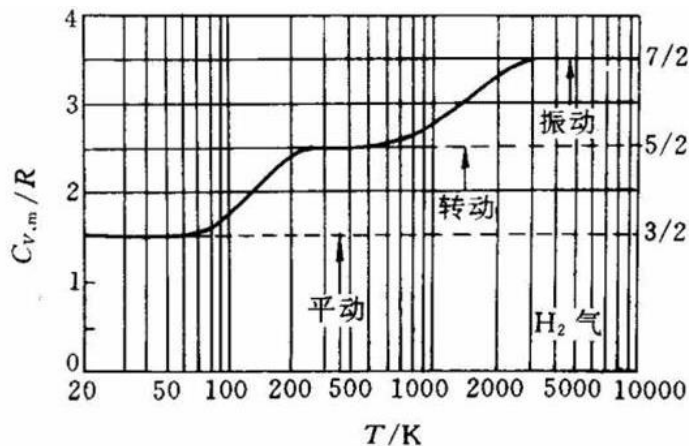


图 2-17 爱因斯坦理论
曲线与金刚石热容量的拟合

$$\varepsilon_l = \frac{l(l+1)}{2J} = l(l+1)k_B\theta_r, g_l = 2l+1$$

$$z = \sum_l g_l e^{-\varepsilon_l/k_B T} \approx 1 + 3e^{-2\theta_r/T}$$

$$\ln z \approx 3e^{-2\theta_r/T}$$

$$E = -N \frac{\partial \ln z}{\partial \beta} \approx 6Nk_B\theta_r e^{-2k_B\theta_r\beta}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \approx 12Nk_B \left(\frac{\theta_r}{T} \right)^2 e^{-2\theta_r/T}$$

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar\omega = \left(n + \frac{1}{2} \right) k_B\theta_V, g_n = 1$$

$$z = \sum_n g_n e^{-\varepsilon_n/k_B T} = \frac{e^{-\theta_V/2T}}{1 - e^{-\theta_V/T}}$$

$$\ln z = -\theta_V/2T - \ln(1 - e^{-\theta_V/T})$$

$$E = -3N \frac{\partial \ln z}{\partial \beta} = 3Nk_B\theta_V/2 + 3N \frac{k_B\theta_V}{e^{\beta k_B\theta_V} - 1}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3Nk_B \left(\frac{\theta_V}{T} \right)^2 \frac{e^{\theta_V/T}}{(e^{\theta_V/T} - 1)^2}$$

二能级系统

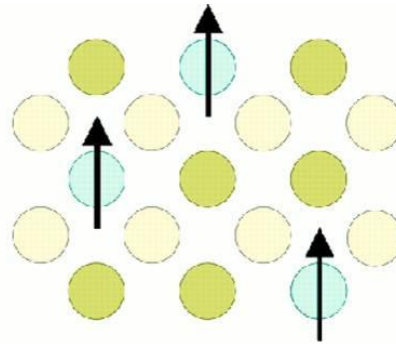
宏观描述

N个磁性原子，温度为T，外加磁场为H，总磁化强度为M，总能量为E，热容为C，熵为S

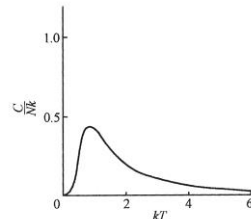
$$\bar{E} = \bar{a}_1 \varepsilon_1 + \bar{a}_2 \varepsilon_2 = -N\varepsilon \frac{e^{\beta\varepsilon} - e^{-\beta\varepsilon}}{e^{\beta\varepsilon} + e^{-\beta\varepsilon}}$$

$$C = \frac{\partial \bar{E}}{\partial T} = Nk_B \left(\frac{\Delta\varepsilon}{k_B T} \right)^2 \frac{1}{\left(e^{\varepsilon/k_B T} + e^{-\varepsilon/k_B T} \right)^2}$$

diluted magnetic semiconductor



Science 14 August 1998:
Vol. 281, no. 5379, pp.
951 - 956



肖特基热容行为

微观描述

ε	ε_i	g_i	a_i	p_i
ε	ε_2	1	a_2	p_2
$-\varepsilon$	ε_1	1	a_1	p_1

$$Z = \sum_i g_i e^{-\beta\varepsilon_i} = e^{\beta\varepsilon} + e^{-\beta\varepsilon}$$

子系配分函数

$$e^{-\alpha} = N/Z \quad \beta = 1/k_B T$$

$$\bar{a}_1 \approx \tilde{a}_1 = 1 \cdot e^{-\alpha - \beta\varepsilon_1} = \frac{Ne^{\beta\varepsilon}}{e^{\beta\varepsilon} + e^{-\beta\varepsilon}}$$

$$\bar{a}_2 \approx \tilde{a}_2 = 1 \cdot e^{-\alpha - \beta\varepsilon_2} = \frac{Ne^{-\beta\varepsilon}}{e^{\beta\varepsilon} + e^{-\beta\varepsilon}}$$

$$p_i = \tilde{a}_i / N = e^{-\varepsilon_i/k_B T} / Z$$

玻尔兹曼因子

麦玻分布的检验与F-D分布、 B-E分布

Bose-Einstein分布与Fermi-Dirac分布

Fermi Gas

Bose Gas

Fermi-Dirac Distribution Law

Bose-Einstein Distribution Law

$$N, E, \{\varepsilon_i\}, \{g_i\}, \{a_i\}$$

$$a_i < g_i, g_i \geq 1, a_i \geq 1$$

History on Fermi-Dirac statistics
In 1926, the Italian physicist Enrico Fermi and the Austrian physicist Paul Dirac independently discovered the Fermi-Dirac statistics, which describes the behavior of particles with half-integer spin (fermions). This discovery was crucial for understanding the structure of matter and the behavior of electrons in solids.

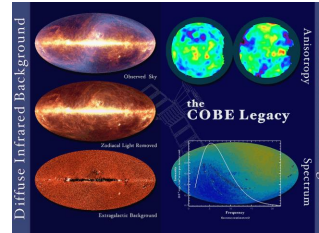
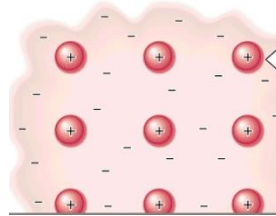
不可分辨
非定域子系

History on Bose-Einstein statistics
In the early 1920s, the Indian physicist Satyendra Nath Bose and the Dutch physicist Albert Einstein independently discovered the Bose-Einstein statistics, which describes the behavior of particles with integer spin (bosons). This discovery was crucial for understanding the behavior of photons and the formation of Bose-Einstein condensates.

$$N, E, \{\varepsilon_i\}, \{g_i\}, \{a_i\}$$

$$g_i \geq 1, a_i \geq 1$$

$$\begin{cases} N = \sum_i a_i \\ E = \sum_i a_i \varepsilon_i \end{cases} \Rightarrow \begin{cases} \sum_i \delta a_i = 0 \\ \sum_i \varepsilon_i \delta a_i = 0 \end{cases}$$



$$\begin{cases} N = \sum_i a_i \\ E = \sum_i a_i \varepsilon_i \end{cases} \Rightarrow \begin{cases} \sum_i \delta a_i = 0 \\ \sum_i \varepsilon_i \delta a_i = 0 \end{cases}$$

$$W = \prod_i \frac{g_i!}{a_i!(g_i - a_i)!}$$

$$\delta \ln W - \alpha \delta N - \beta \delta E = 0$$

可分辨
定域子系

$$W = \prod_i \frac{(g_i + a_i - 1)!}{a_i!(g_i - 1)!} = \prod_i \frac{(g_i + a_i)!}{a_i!(g_i)!}$$

Maxwell-Boltzmann Distribution Law

$$\tilde{a}_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1}$$

$$W = N! \prod_i \frac{g_i^{a_i}}{a_i!} \quad \left(W = \prod_i \frac{g_i^{a_i}}{a_i!} \right)$$

$$\tilde{a}_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} - 1}$$

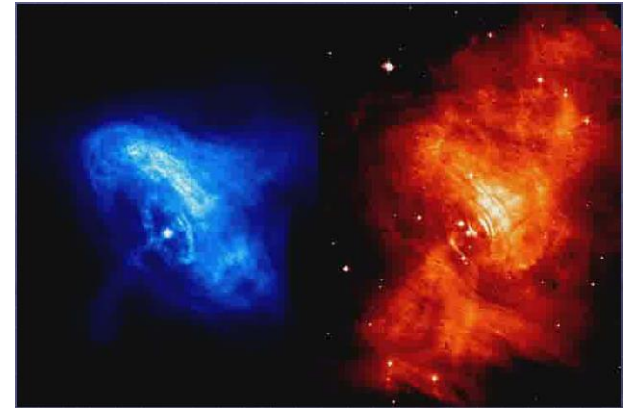
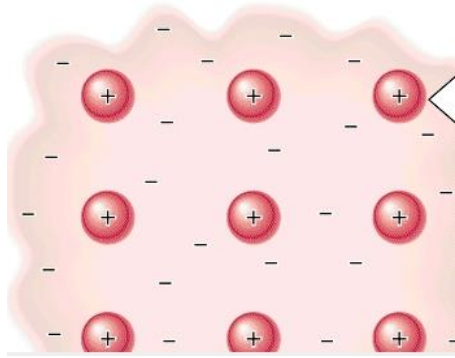
非简并
 $e^{\alpha} \ll 1$

$$\tilde{a}_i = g_i e^{-\alpha - \beta \varepsilon_i}$$

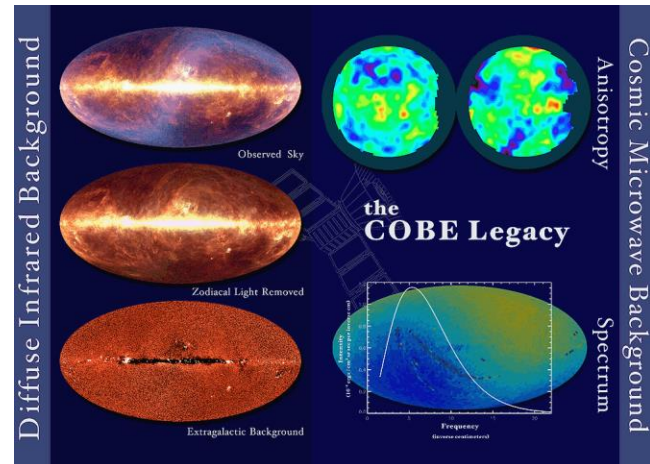
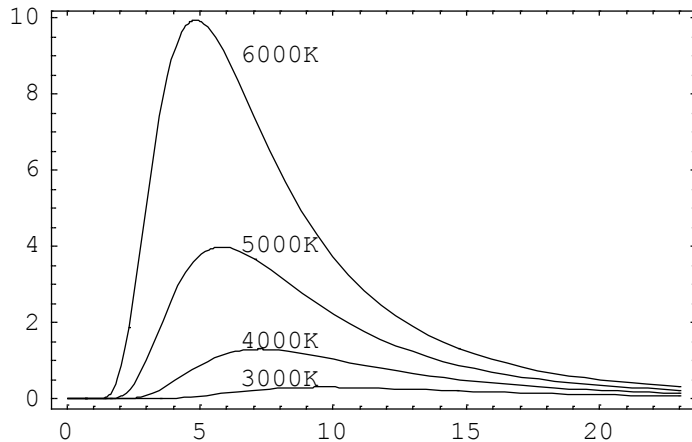
非简并
 $e^{\alpha} \ll 1$

量子气体

- 费米气体：金属中的自由电子气体、白矮星、中子星



- 玻色气体：光子气体、声子气体



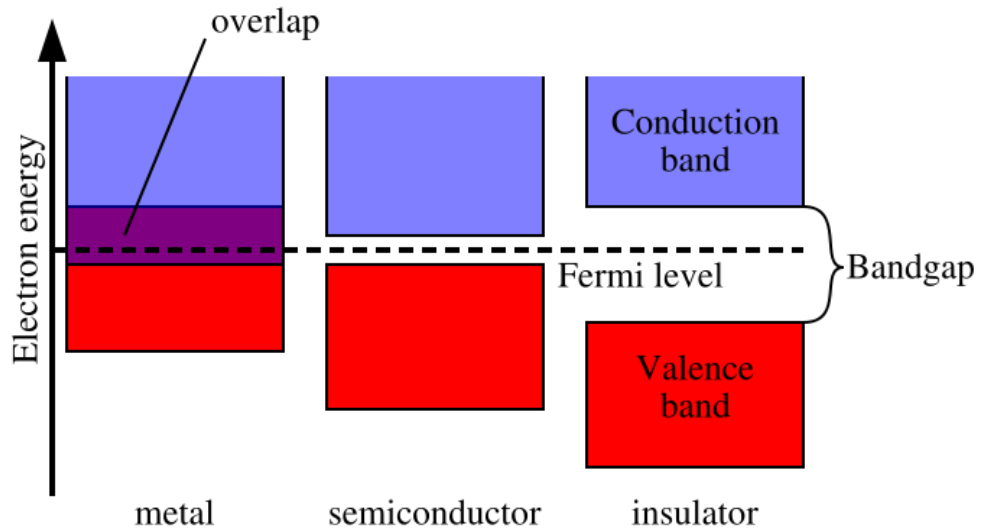
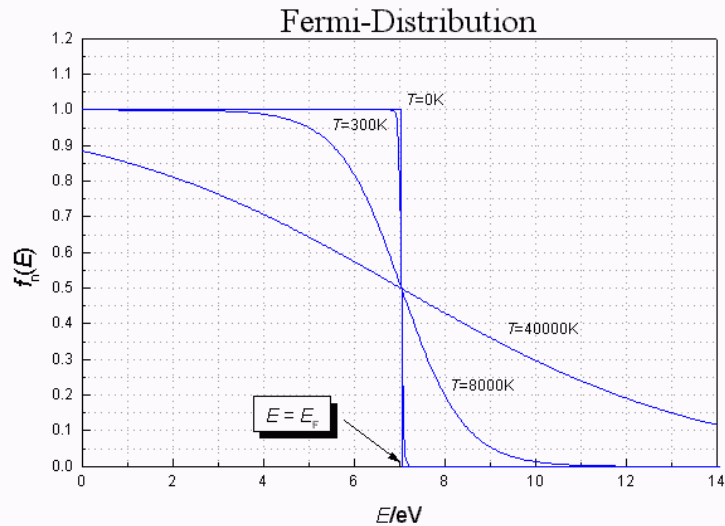
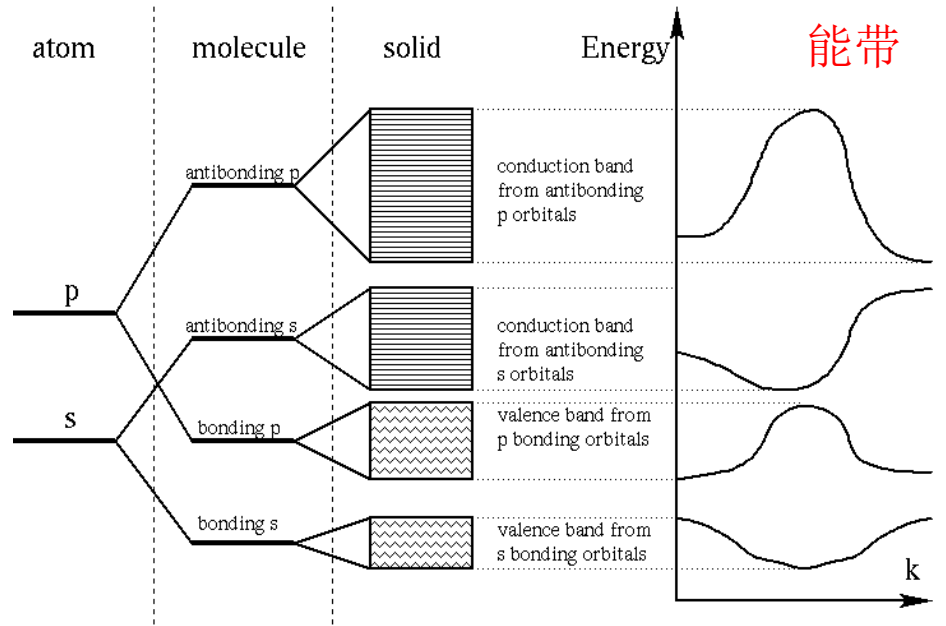
Fermi能级

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}$$

$T \rightarrow 0 \rightarrow$

$$\begin{cases} 0 & \varepsilon > \mu \\ 1 & \varepsilon < \mu \end{cases}$$

陆果，《基础物理学》，下卷，P941-951

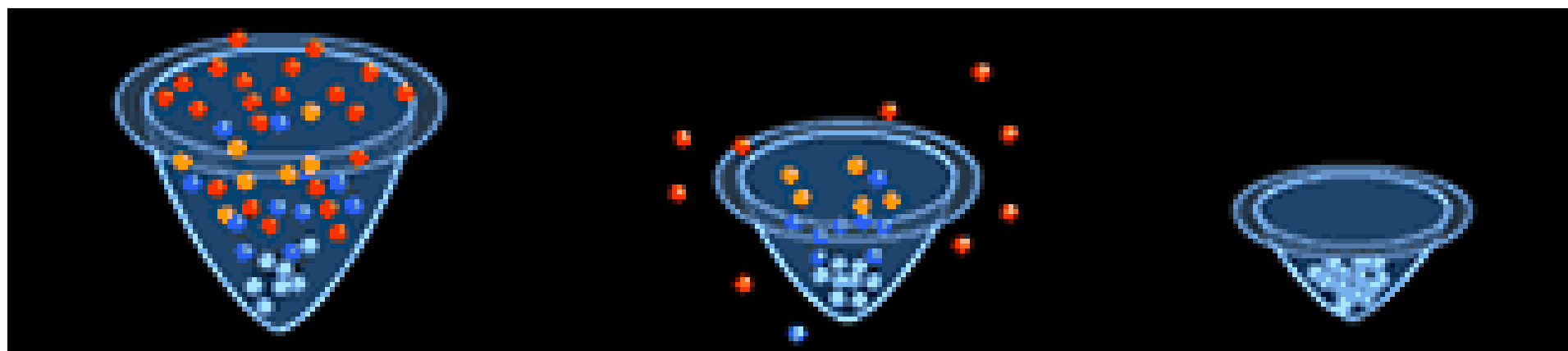


Bose-Einstein 凝聚

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} - 1} \Rightarrow n(0) = \frac{1}{e^{(\varepsilon_0-\mu)/k_B T} - 1}$$

$$\frac{n_a}{n_0} = \frac{e^{(\varepsilon_0-\mu)/k_B T} - 1}{e^{(\varepsilon_a-\mu)/k_B T} - 1} \leq \frac{e^{(\varepsilon_0-\mu)/k_B T}}{e^{(\varepsilon_a-\mu)/k_B T}} = e^{(\varepsilon_0-\varepsilon_a)/k_B T} \xrightarrow{T \rightarrow 0} 0$$

发生凝聚
相变后，
液He的超
流动性、
电子的超
导性、凝
聚原子的
相干性



气体分子的碰撞与扩散

作业

- 4.8, 4.12

气体分子的碰撞：平均碰撞频率、平均自由程

香水扩散

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T \Rightarrow v \approx 500 \text{ m/s}$$

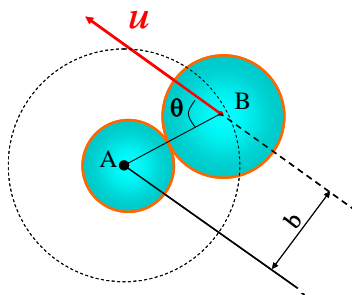
系统通过碰撞
达到平衡态

碰撞及其描述

瞄准距离 b

有效碰撞截面

$$\sigma = \pi d^2$$



两分子靠近时运动方向发生明显改变的瞄准距离作为有效碰撞截面的直径

温度高，有效碰撞截面 σ 小

两个刚性球的碰撞演示

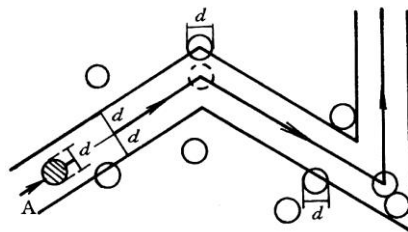
分子随自由程的概率分布

$$1/\bar{\lambda} \quad dl/\bar{\lambda}$$

$$-dN = N(l) - N(l + dl) = \frac{Ndl}{\bar{\lambda}}$$

$$\frac{dN}{N} = -\frac{dl}{\bar{\lambda}}$$

$$N(l=0) = N_0 \quad \boxed{P(l) = N/N_0 = e^{-l/\bar{\lambda}}}$$



自由程, λ

碰撞频率, Z

平均碰撞频率

$$\bar{v} = \bar{\lambda} \cdot Z$$

平均自由程

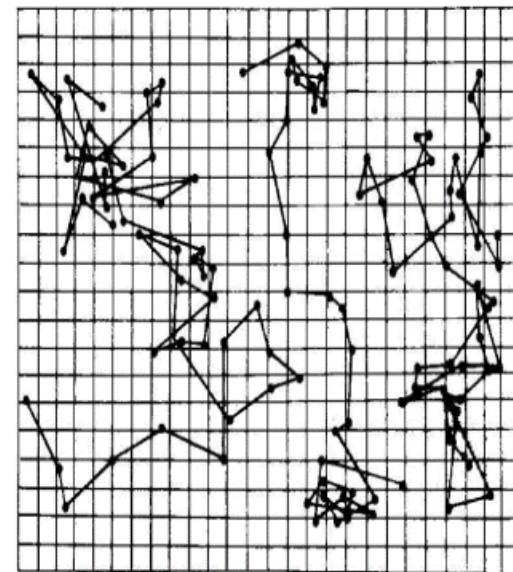
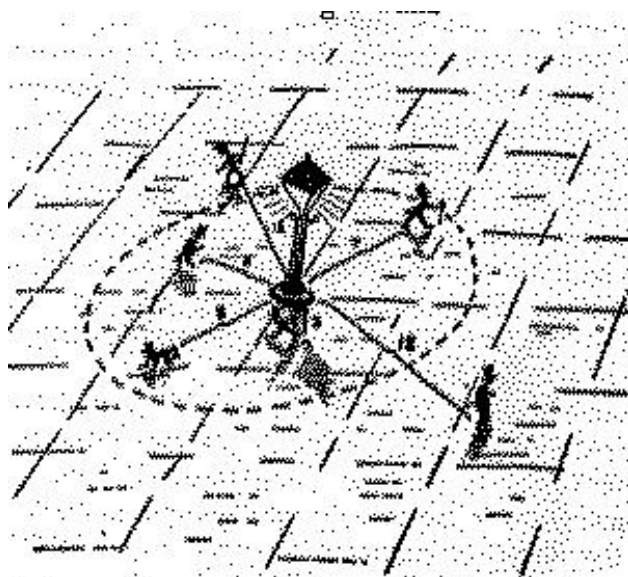
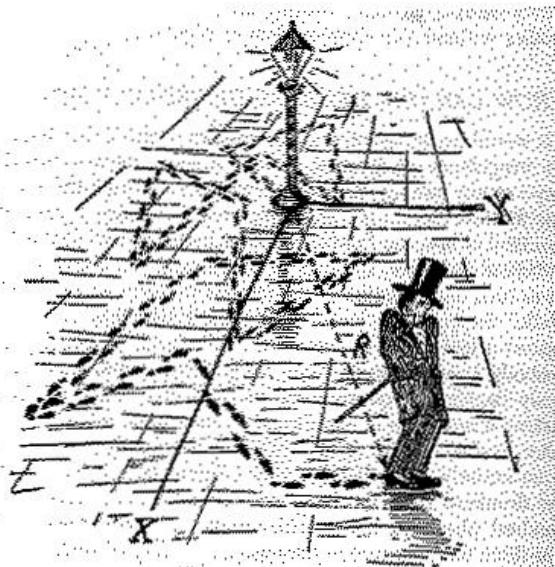
$$\bar{Z} = \frac{\pi d^2 \bar{u} \Delta t n}{\Delta t} = \sigma \bar{u} n$$

$$\bar{u} = \sqrt{2} \bar{v}$$

包科达《热物理学基础》P322-323

$$\boxed{\bar{\lambda} = \frac{1}{\sqrt{2} \sigma n}}$$

气体分子的扩散：醉汉无规随机行走、布朗运动



$$X_i^2 + Y_i^2 = 1$$

$$R^2 = \left(\sum_{i=1}^M X_i \right)^2 + \left(\sum_{i=1}^M Y_i \right)^2$$

$$m \frac{d^2 \vec{r}}{dt^2} = -6\pi a \eta \frac{d\vec{r}}{dt} + \vec{F}(t)$$

$$\begin{aligned} & (X_1 + X_2 + \dots + X_M)^2 \\ &= X_1^2 + X_1 X_2 + X_1 X_3 \dots + X_2^2 + X_1 X_2 + \dots + X_M^2 \end{aligned}$$

$$\frac{m}{2} \frac{d^2 \overline{(s^2)}}{dt^2} - k_B T = -3\pi a \eta \frac{d \overline{(s^2)}}{dt}$$

\mathbf{x}_i 完全随机, \mathbf{x}_i 与 \mathbf{x}_j 完全独立. $\langle X_i \rangle = 0, \langle X_i X_j \rangle = 0$

$$a \approx 10^{-6} m, \eta = 10^{-3} \text{ Kg} / (m \cdot s)$$

$$\text{air } \eta = 1.81 \times 10^{-5} \text{ Kg} / (m \cdot s)$$

$$R^2 = \sum_{i=1}^M (X_i^2 + Y_i^2) = M$$

$$R = \sqrt{M}$$

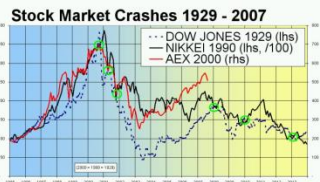
$$\overline{s^2} = \frac{k_B T}{3\pi a \eta} t = 2Dt$$

气体的运输过程

作业

- 4.18, 4.21

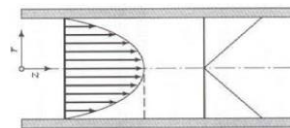
气体中的运输过程



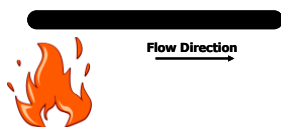
非平衡态 → 近平衡态 → 运输过程

↑ 偏离平衡态不远的系统

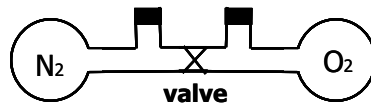
局域平衡假设，即假设系统由一系列达到平衡态的微元组成，对整个系统的描述就是由对每一个平衡态微元的描述而组成的



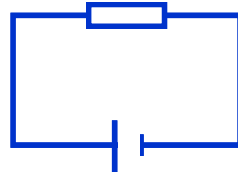
粘滞现象



热传导现象



扩散现象



电流

Direct and Coupled Transport Phenomena

	TEMPERATURE GRADIENT	PRESSURE GRADIENT	CHEM. POTENTIAL GRADIENT
HEAT FLUX	Thermal Conductivity	Thermal Filtration (Condensation/evaporation) <small>small</small>	Dufour Effect <small>small</small>
FLUID FLUX	Thermal Osmosis (Vapor transport)	Pressure Advection (Saturated & unsat. hydraulic conduct)	Osmotic Flow (Osmotic efficiency) (Vapor transport)
SALT FLUX	Soret Effect <small>small</small>	Hyperfiltration (Reverse osmosis) (Osmotic efficiency)	Chemical Diffusion

