

现代物理学概论

1. 热力学第二定律
2. “熵”的起源

对自然界(宇宙)的基本看法/研究方法:

一切归结为最基本的组成单元和决定单元行为的最基本规律。

--还原论 (Reductionism)

“最终目的”是建立一个包罗万象的 “大统一理论” - Grand Unification Theory

指数墙带来的困惑

由基本的相互作用力就能推出自然界的所有规律吗？

这是“大统一理论”的追求目标，但答案是否定的。



Walter Kohn
Nobel化学奖

指数墙问题

实际材料中原子数 $N \sim 10^{23}$

系统总的自由度数不是每个粒子自由度数相加，而是相乘！



自由度随粒子数指数增加

对自然界(宇宙)的另一种看法/研究方法:

客观世界是分层次的，每个层次都有自己的基本规律，重要的是承认客观现实，以它为依据，找出它的基本规律，理解这些现象是如何“演生”出来的。

--演生论 (Emergence) / 整体论 (Whoism)

演生论与还原论这两者是对立的，但又是互补的！



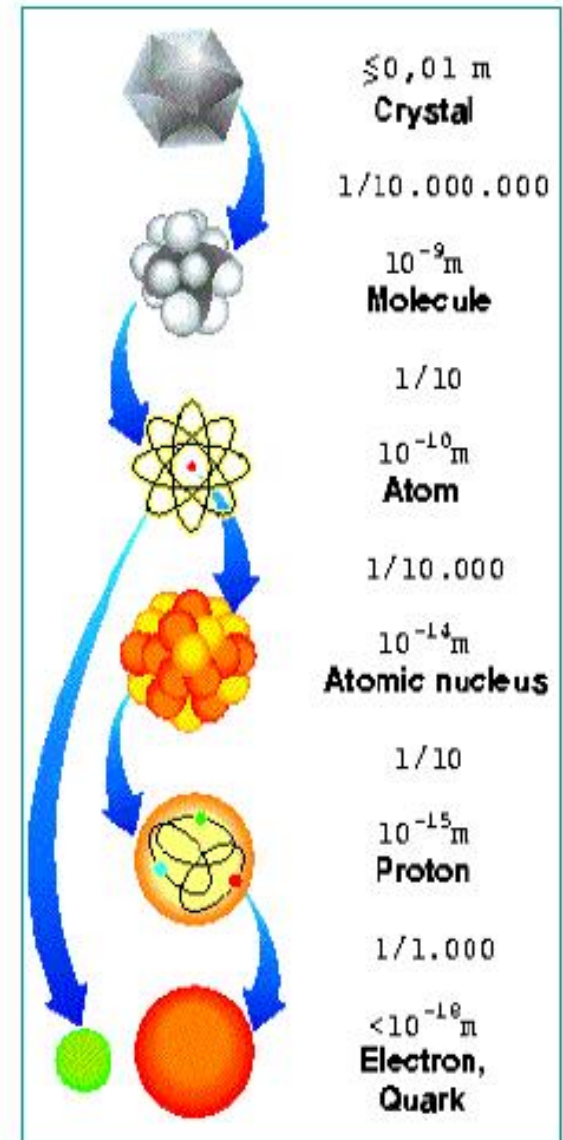
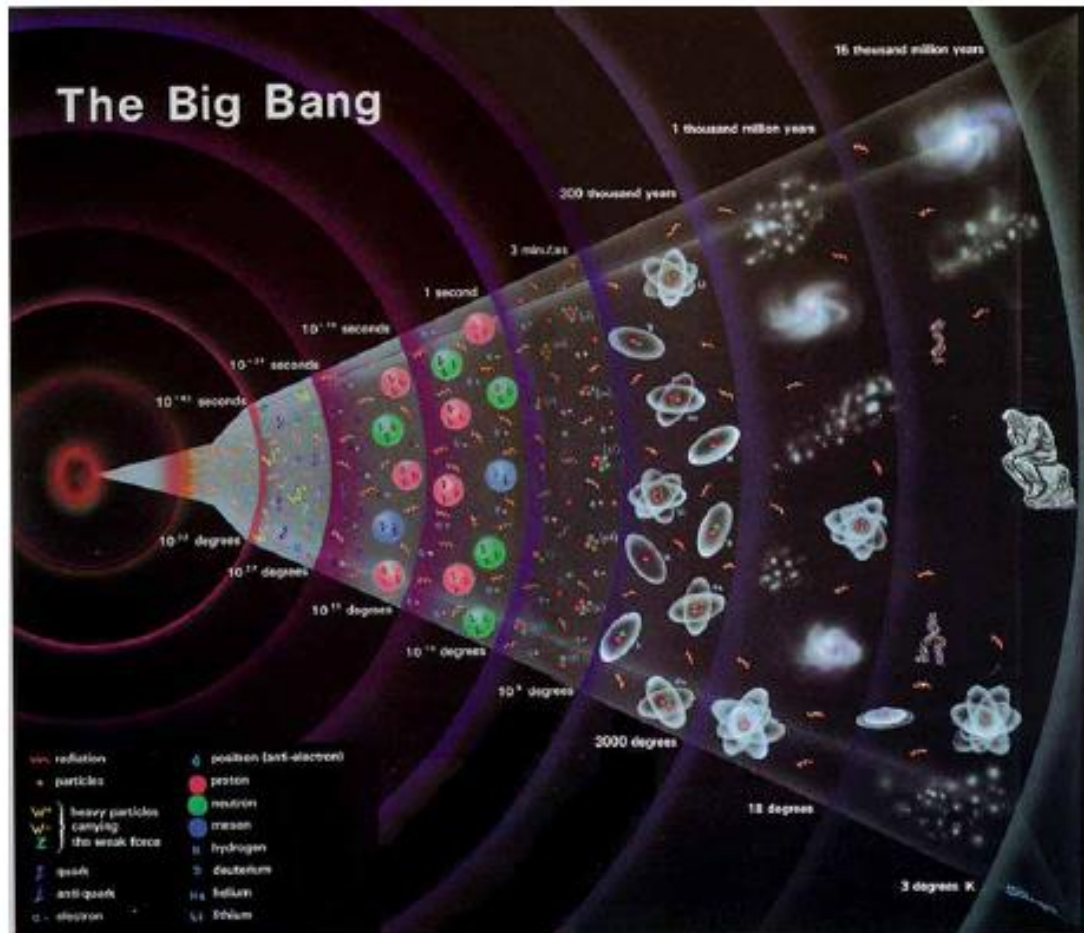
Philip W. Anderson: More is different (1972)

更多是不同的

……将万事万物还原成简单的基本规律，并不蕴含着从这些规律出发重建宇宙的能力……

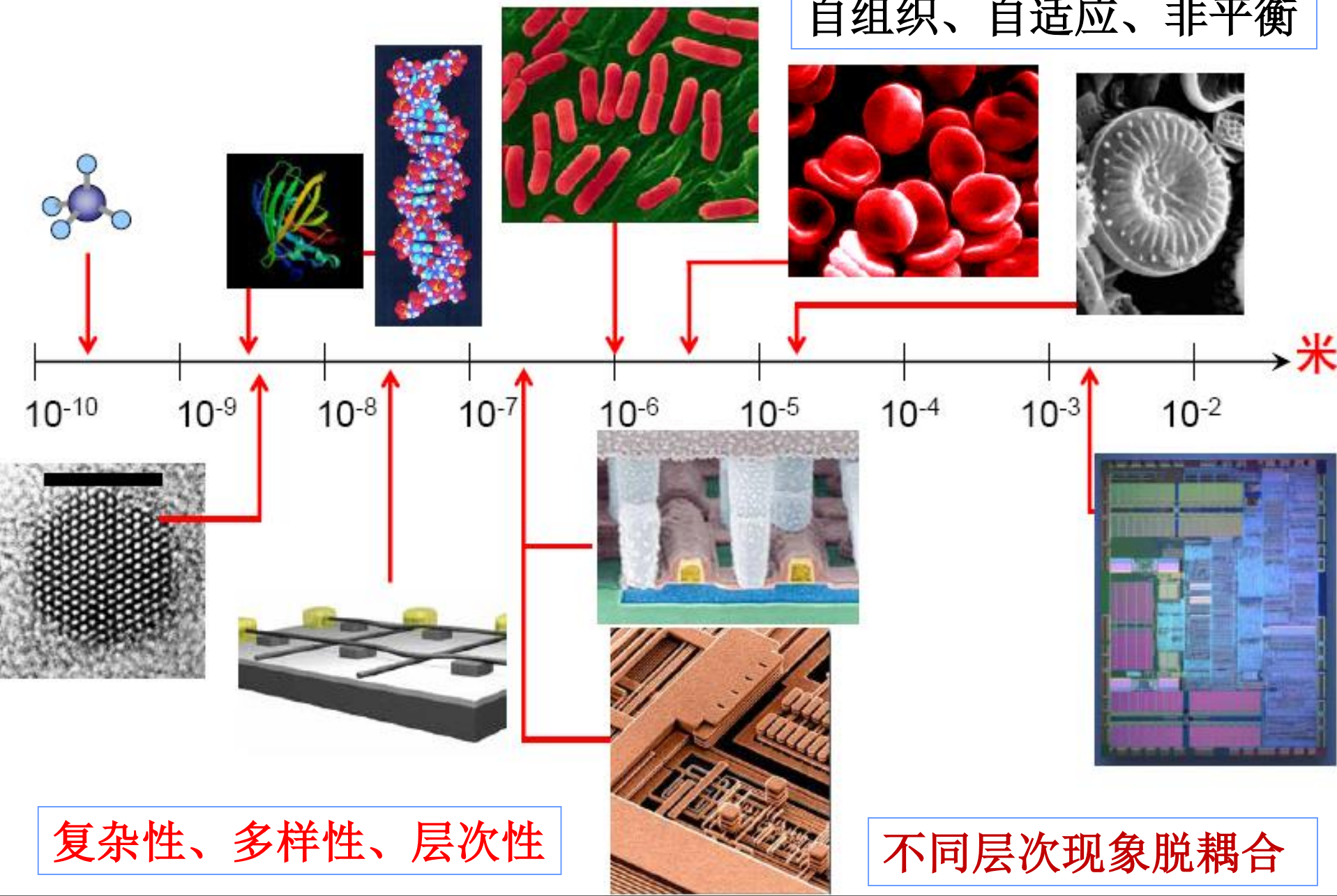
面对尺度与复杂性的双重困难，重建论的假定就崩溃了。不能依据少数粒子的性质作简单外推来解释由大量粒子构成的复杂集聚体的行为。正好相反，在复杂性的每一个层次会呈现全新的性质，为理解这些新行为所需要作的研究，就其基础性而言，与其他研究相比毫不逊色。

The universe is emerged !



More Is Different!

自组织、自适应、非平衡

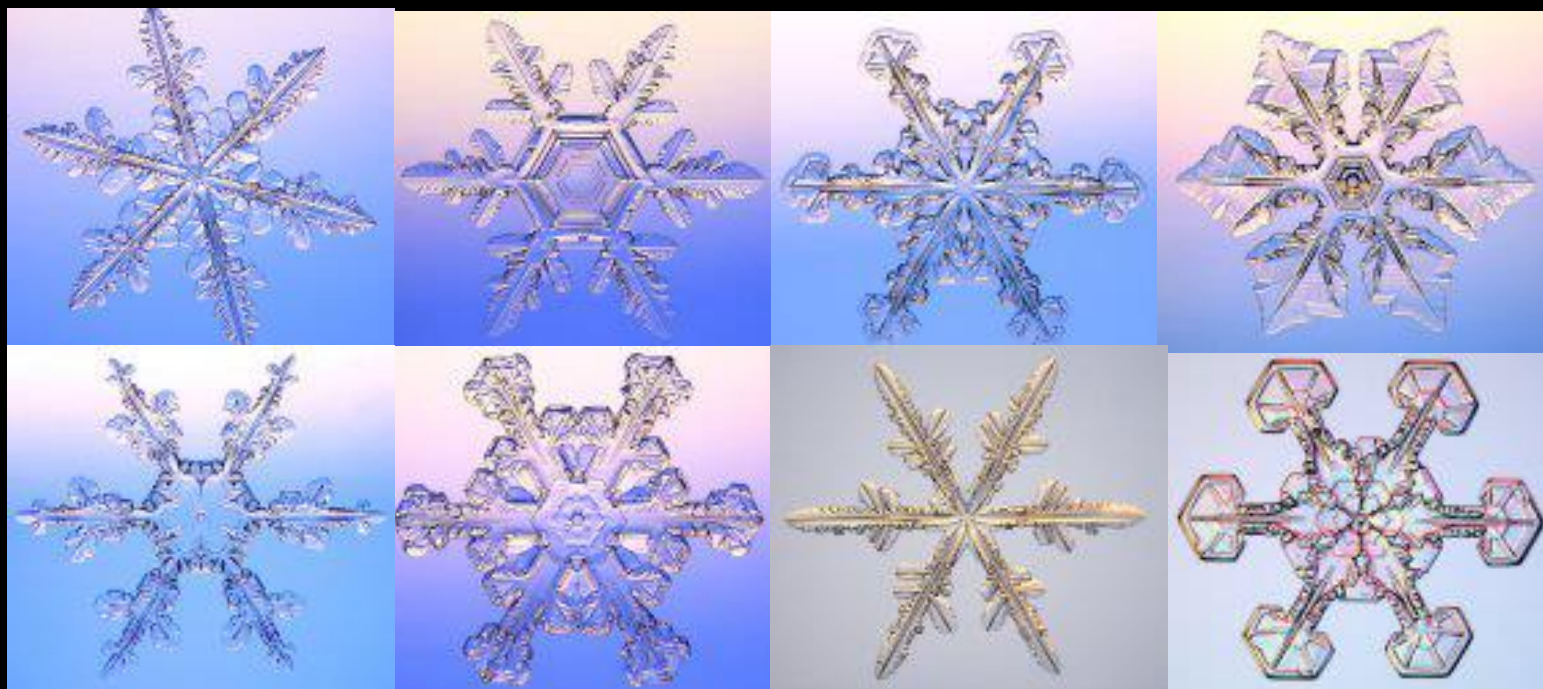


从水的三态变化

100° C 水沸腾成蒸汽

0° C 水冻结成冰

仔细想想，为什么 10^{23} 个水分子，单个水分子结构不变、相互作用不变，会“集体地”、“不约而同地”从一个相“变”到另一个相呢？“新相”在“老相”中如何“孕育”、“形成”，如何“呈展”？



“热”究竟是什么？

热量 = 能量！

- Heat is energy that is transferred from one body to another because of a difference in temperature.

(1842)

- $dU = dQ + dW$

用热做功是否存在限制？
——“熵”的起源

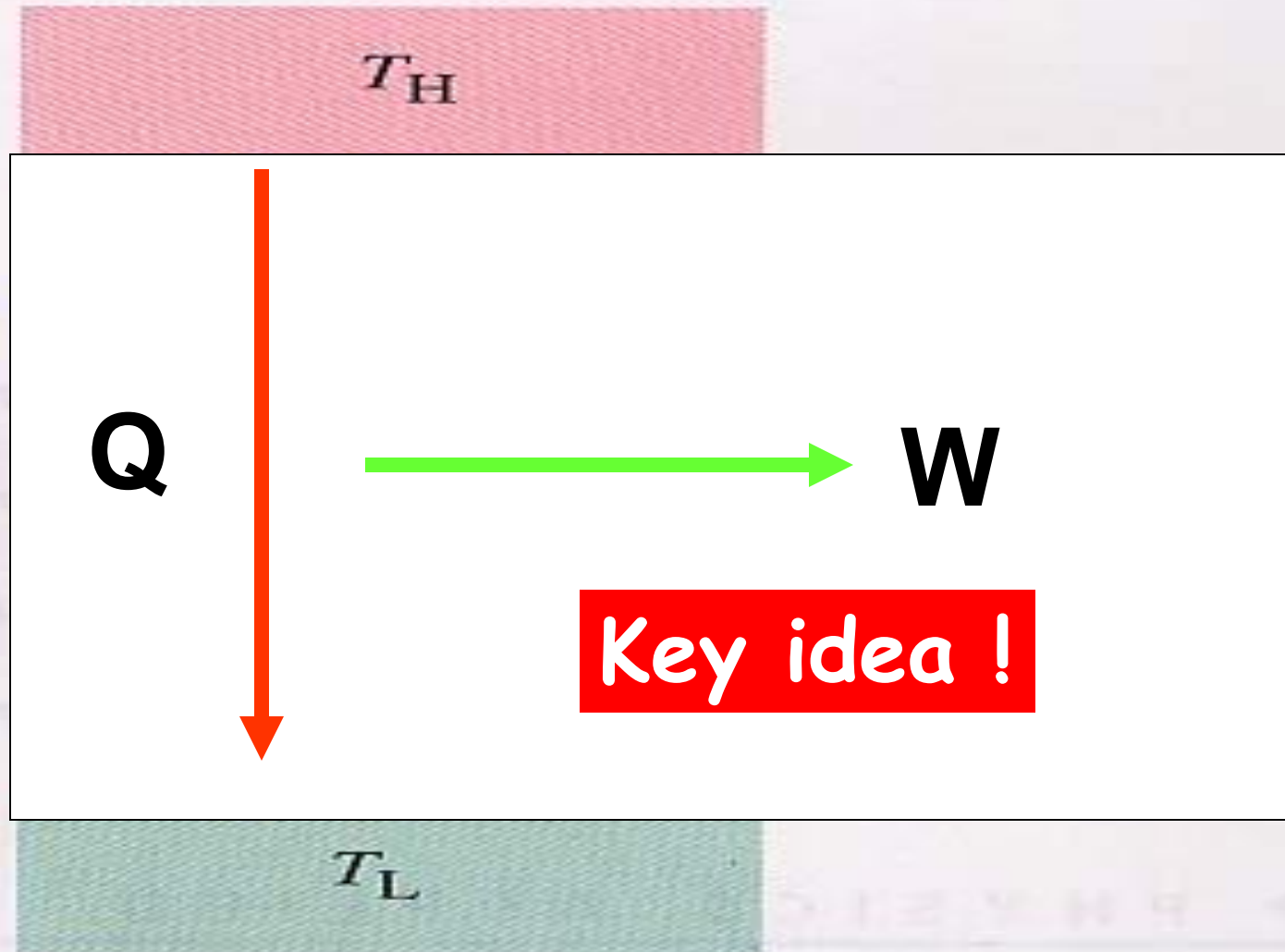
卡 诺

Sadi Carnot

卡诺循环



Carnot's ideas



Carnot's theorem

"All **reversible** engines operating between the same two constant temperatures T_H and T_L have the same efficiency.

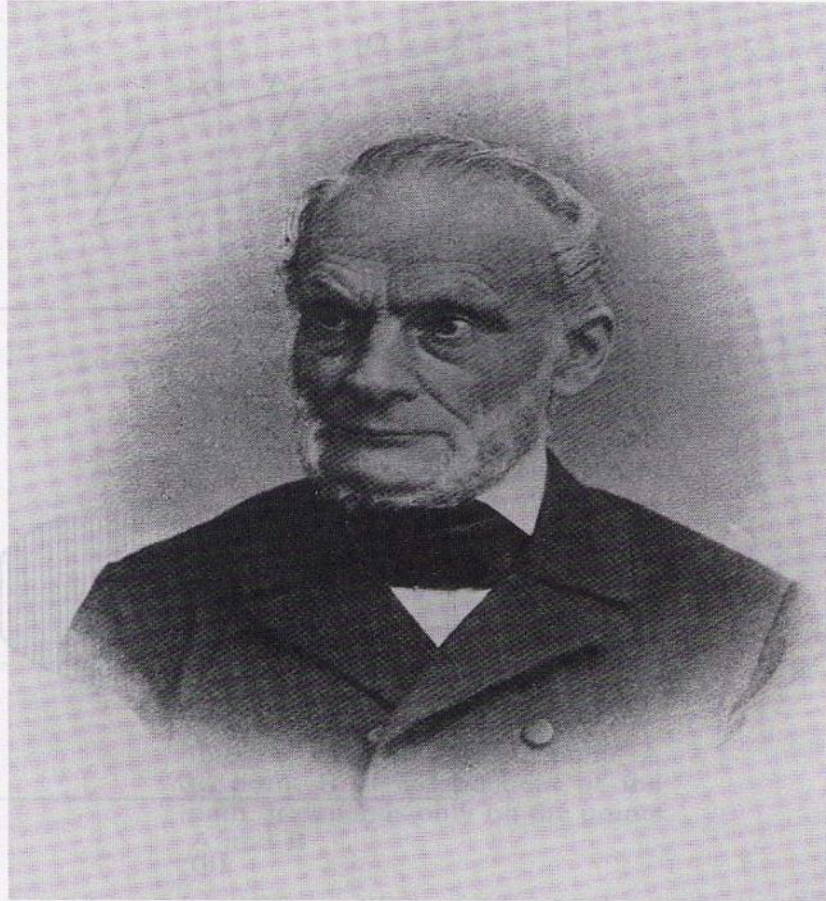
$$e = W / Q_H = 1 - Q_L / Q_H = 1 - T_L / T_H$$

Any **irreversible** engine operating between the same two fixed temperatures will have an efficiency **less than this.**"

克劳修斯

R. Clausius

熵的引入



Rudolf Clausius (1822–1888) (Courtesy the E. F. Smith Collection, Van Pelt-Dietrich Library, University of Pennsylvania)

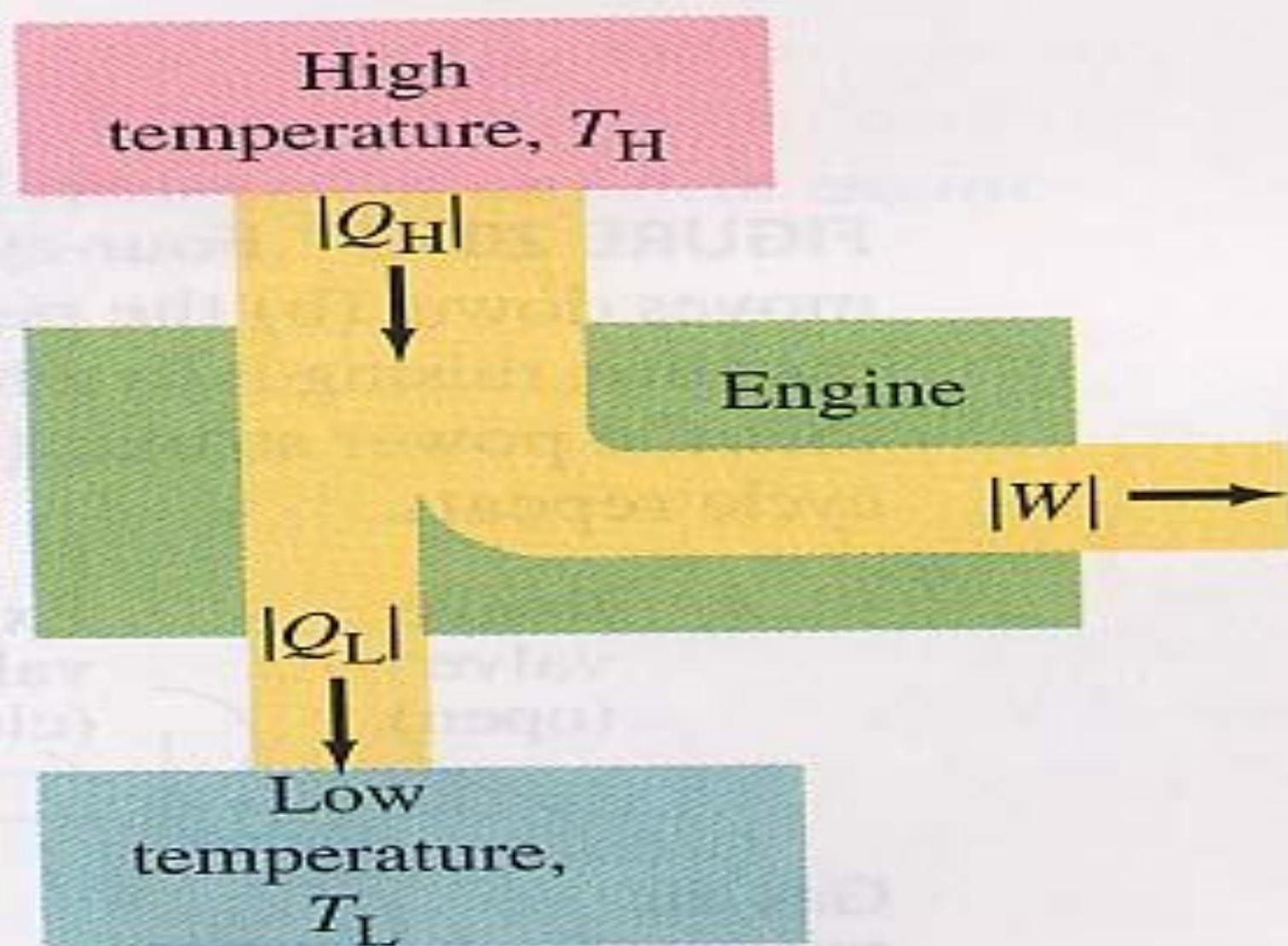


FIGURE 20–1 Schematic diagram of energy transfers for a heat engine.

Clausius' deduction (1865)

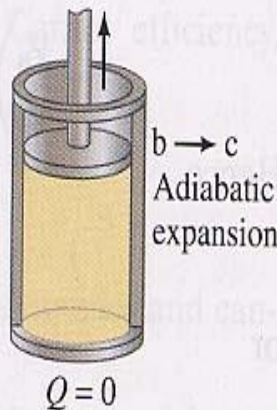
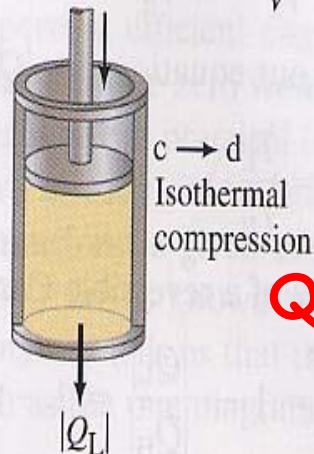
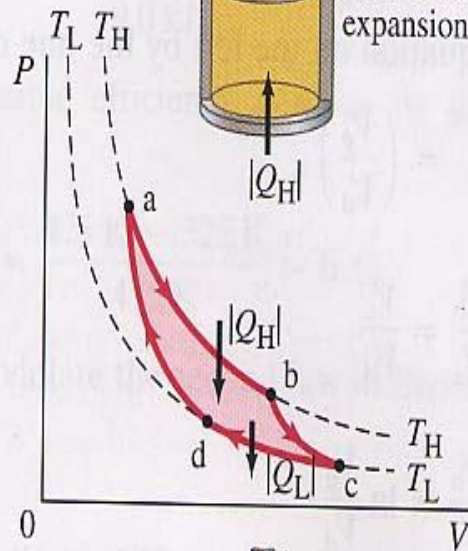
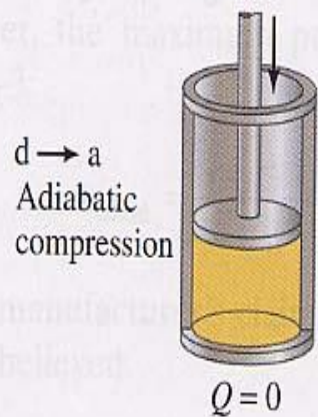
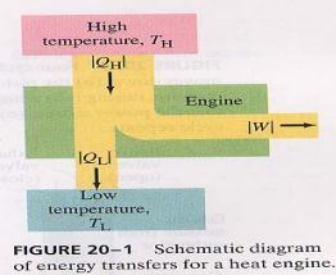


FIGURE 20-5 The Carnot cycle. Heat engines work in a cycle, and the cycle for the Carnot engine begins at point a on this PV diagram. (1) The gas is first expanded isothermally, with the addition of heat $|Q_H|$, along the path ab at temperature T_H . (2) Next the gas expands adiabatically from b to c—no heat is exchanged, but the temperature drops to T_L . (3) The gas is then compressed at constant temperature T_L , path c to d, and heat $|Q_L|$ flows out. (4) Finally, the gas is compressed adiabatically, path da, back to its original state. No Carnot engine actually exists, but as a theoretical engine it played an important role in the development of thermodynamics.

$$e = W / Q_H$$

$$= 1 - Q_L / Q_H$$

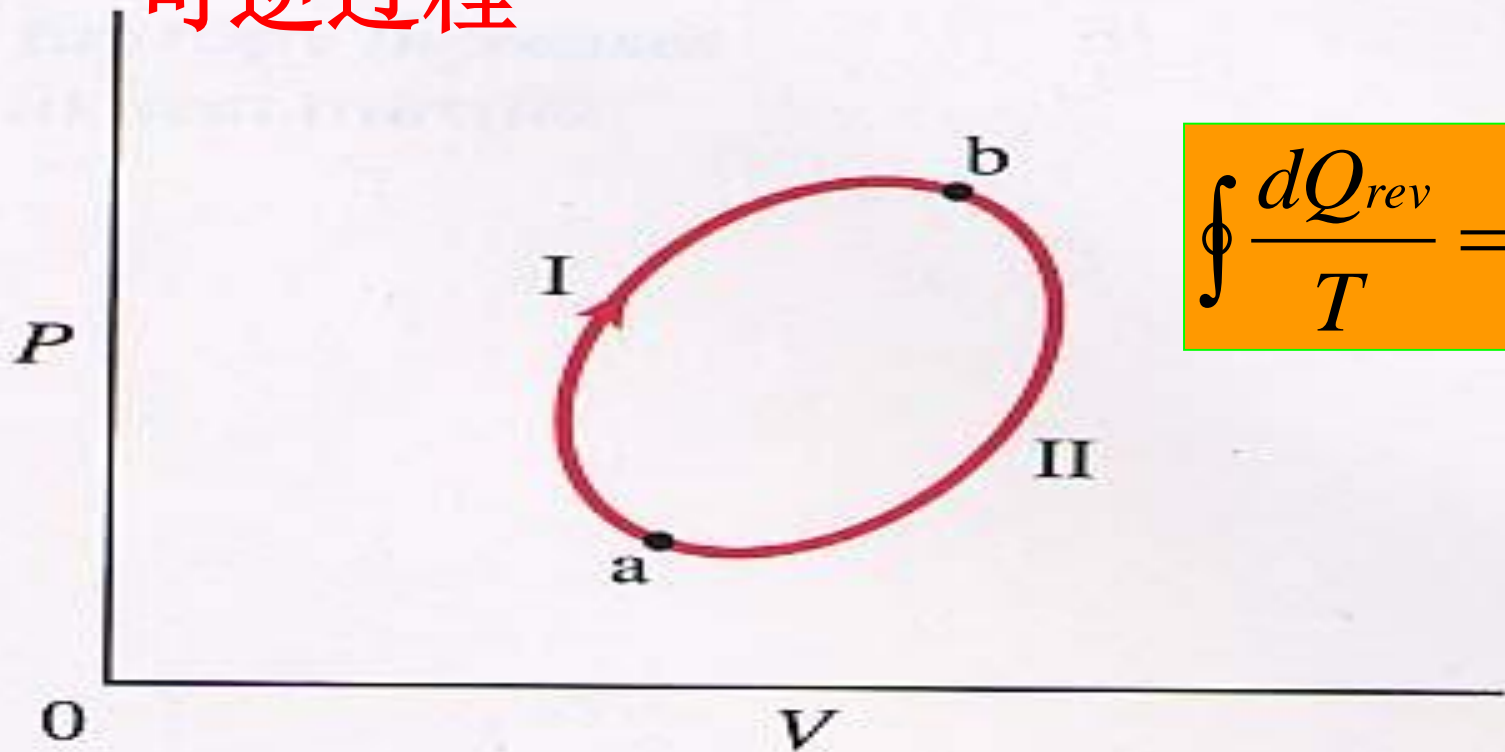
$$= 1 - T_L / T_H$$

$$Q_L / T_L = Q_H / T_H, \quad Q_H / T_H - Q_L / T_L = 0$$

$$\Sigma(Q/T) = 0$$

$$\oint \frac{dQ_{rev}}{T} = 0$$

可逆过程

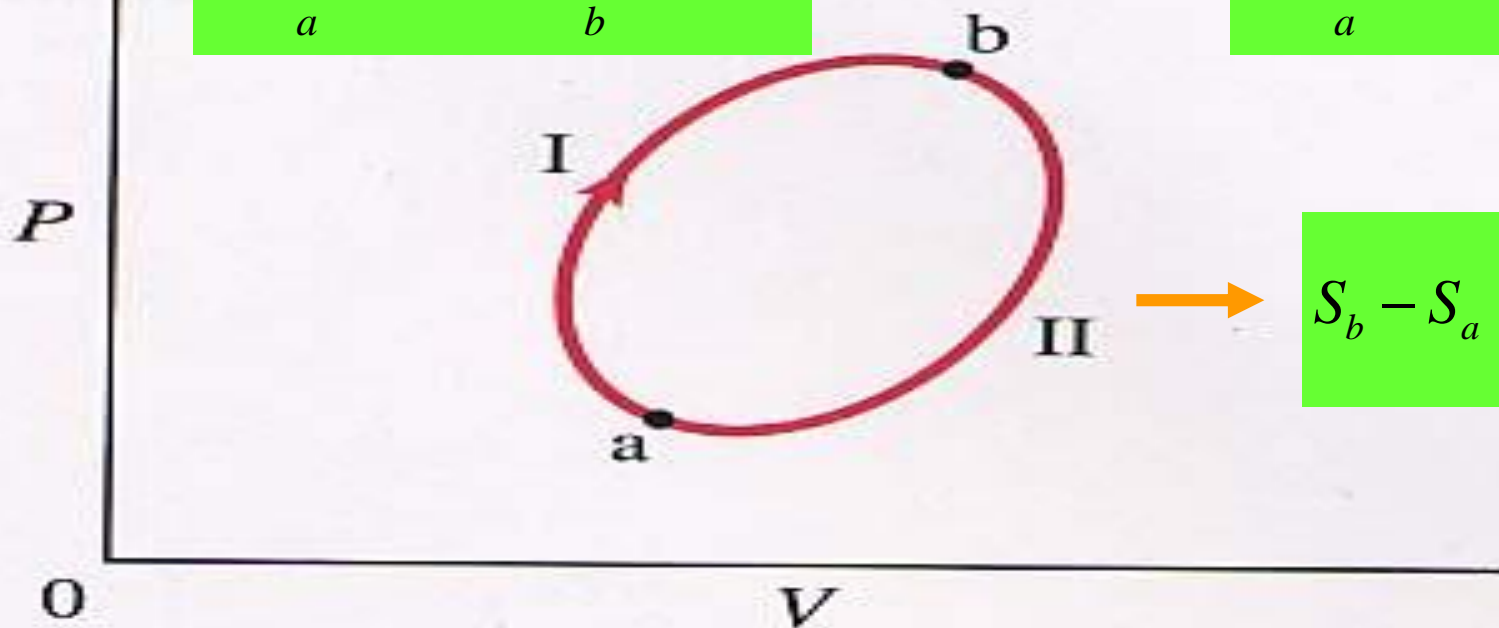


$$\oint \frac{dQ_{rev}}{T} = 0$$

FIGURE 20–12 The integral, $\oint dS$, of the entropy for a reversible cycle is zero. Hence the difference in entropy between states a and b, $S_b - S_a = \int_a^b dS$, is the same for path I as for path II.

$$(I) \int_a^b \frac{dQ}{T} + (II) \int_b^a \frac{dQ}{T} = 0$$

$$(I) \int_a^b \frac{dQ}{T} = (II) \int_a^b \frac{dQ}{T}$$



$$S_b - S_a = \int_a^b \frac{dQ}{T}$$

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$$dS = \frac{dQ}{T}$$

两状态的熵差不依赖具体过程

Irreversible: $e = W / Q_H = 1 - Q_L / Q_H < 1 - T_L / T_H$

不可逆过程

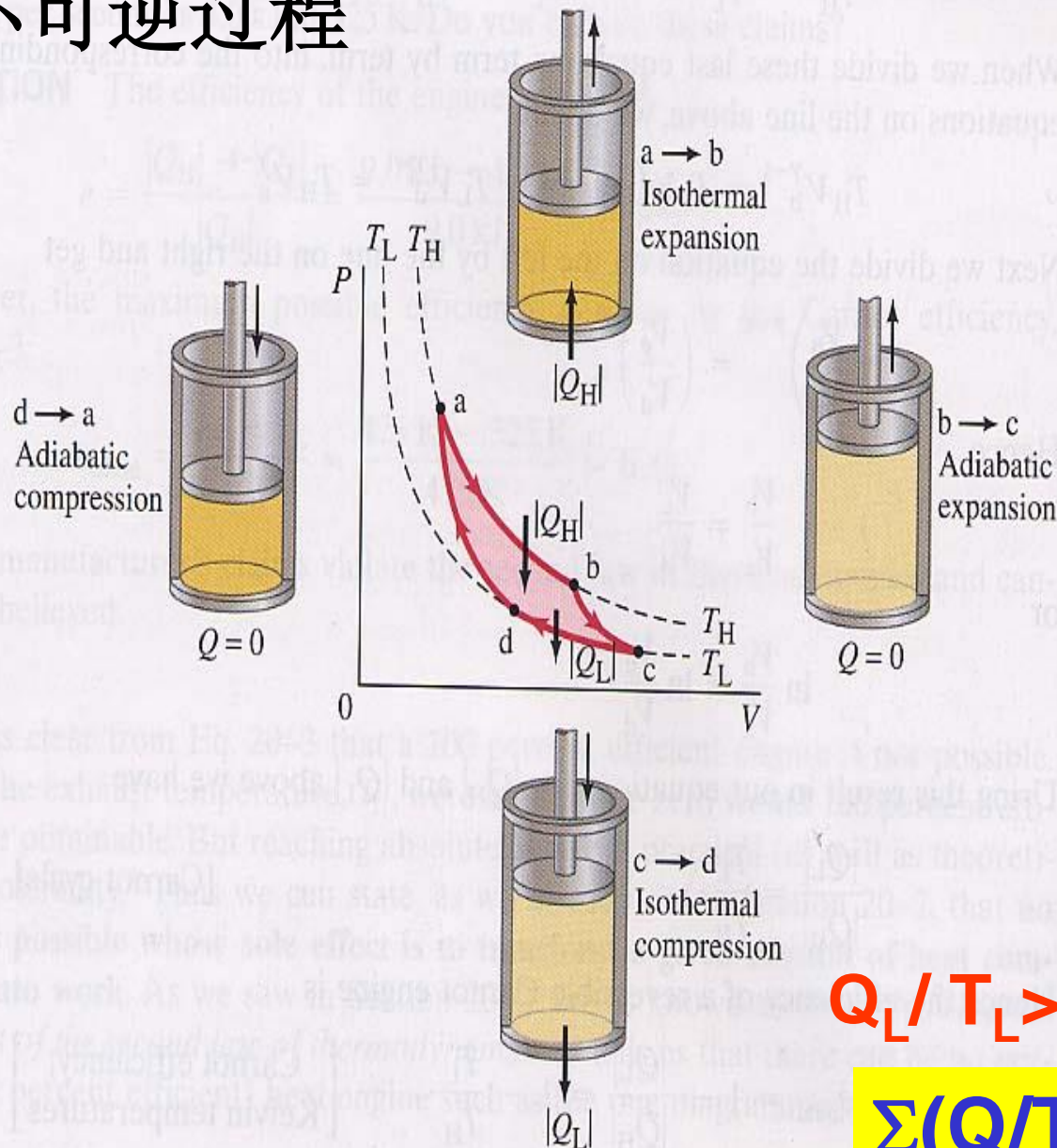


FIGURE 20-5 The Carnot cycle. Heat engines work in a cycle, and the cycle for the Carnot engine begins at point a on this PV diagram. (1) The gas is first expanded isothermally, with the addition of heat $|Q_H|$, along the path ab at temperature T_H . (2) Next the gas expands adiabatically from b to c—no heat is exchanged, but the temperature drops to T_L . (3) The gas is then compressed at constant temperature T_L , path c to d, and heat $|Q_L|$ flows out. (4) Finally, the gas is compressed adiabatically, path da, back to its original state. No Carnot engine actually exists, but as a theoretical engine it played an important role in the development of thermodynamics.

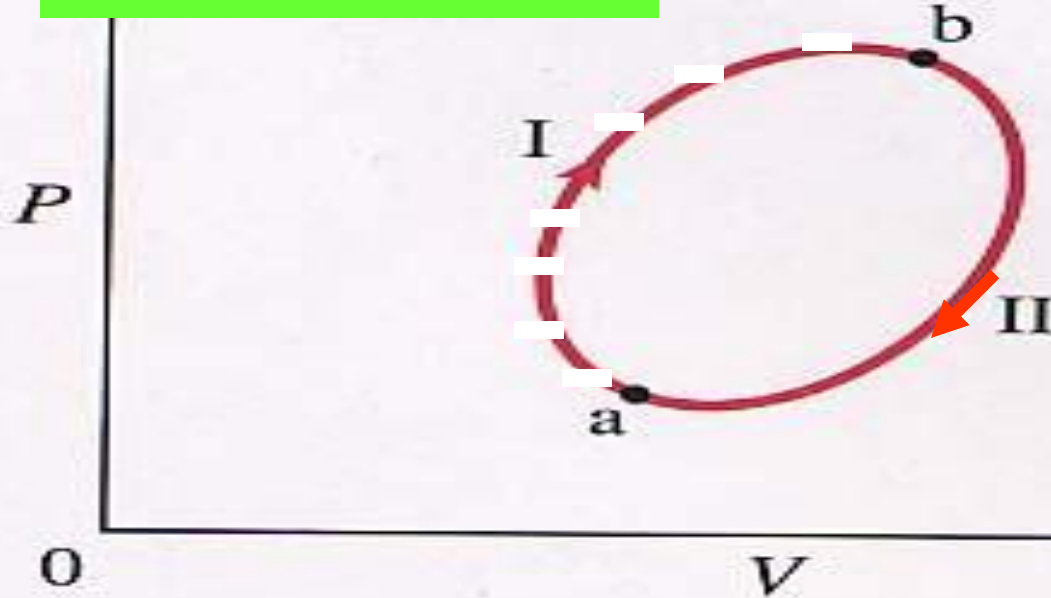
$$Q_L / T_L > Q_H / T_H$$

$$\Sigma(Q/T) < 0$$

$$\oint \frac{dQ_{ir}}{T} < 0$$

$$(I) \int_a^b \frac{dQ}{T} + (II) \int_b^a \frac{dQ}{T} < 0$$

$$(I) \int_a^b \frac{dQ}{T} < (II) \int_a^b \frac{dQ}{T}$$



$$S_b - S_a > \int_a^b \frac{dQ}{T}$$

R&IR

For an isolated system: $\Delta S \geq 0$

$$S_b - S_a \geq \int_a^b \frac{dQ}{T}$$

可逆(I)和不可逆(II)过程的熵变比较

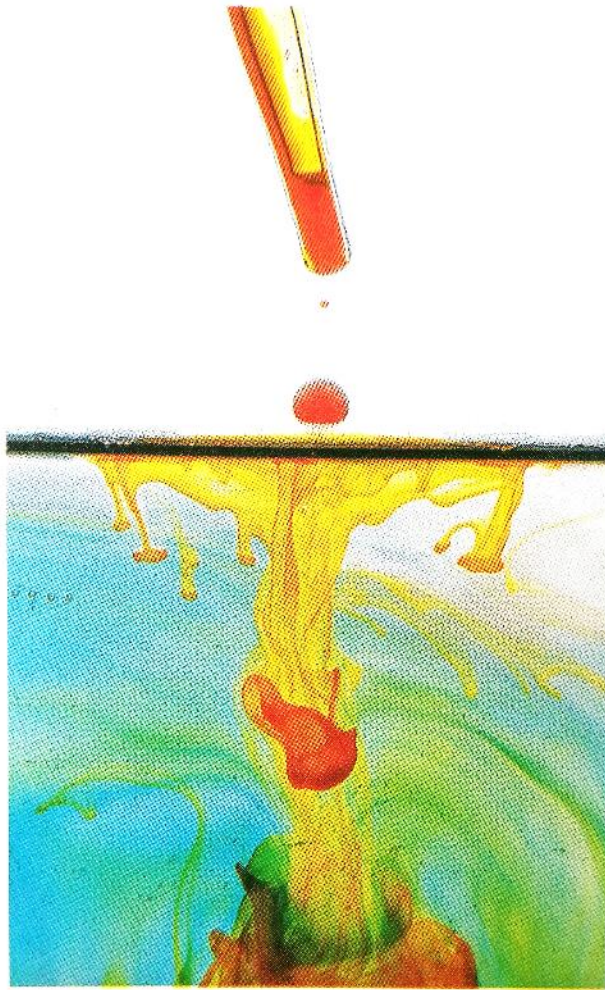
Clausius' Statement

"The energy of the universe is a constant. The entropy of the universe approaches a maximum."

Maxwell (1870)

The 2nd law of thermodynamics has the same degree of truth as the statement that if you throw a tumblerful of water into the sea, you cannot get the same tumblerful out of the water again.

宏观物理过程的不可逆性！



热力学过程不可逆！

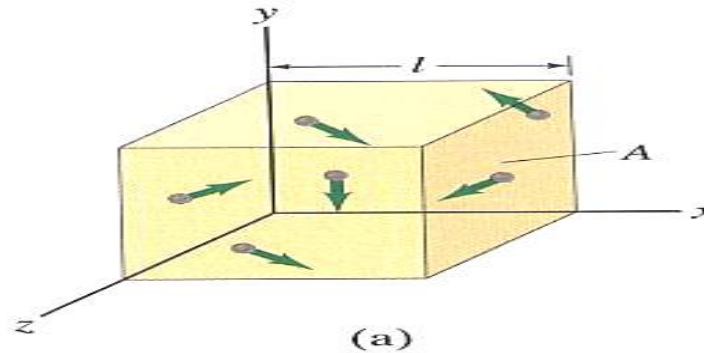
20.17 The mixing of colored ink and water starts from a state of relative order (low entropy) in which each fluid is separate and distinct from the other. The final state after mixing is more disordered (has greater entropy). Spontaneous unmixing of the ink and water, a process in which there would be a net decrease in entropy, is never observed.

Maxwell分布与Boltzmann原理

Where a gas pressure comes from ?

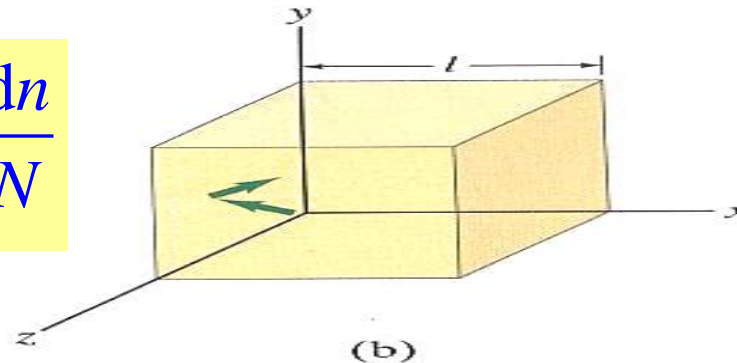
$$\begin{aligned}\overline{v^2} &= \frac{v_1^2 + v_2^2 + \dots + v_N^2}{N} \\ &= \frac{n_1 v_1'^2 + n_2 v_2'^2 + \dots}{N}\end{aligned}$$

$$= \sum_i v_i'^2 \left(\frac{n_i}{N} \right) \rightarrow \int v^2 \frac{dn}{N}$$



Clausius (1857)

$$P = \frac{1}{3} nm \overline{v^2}$$



Maxwell (1860)

$$\frac{dn(v_x, v_y, v_z)}{N} = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left[-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T} \right] dv_x dv_y dv_z$$

Let N be the whole number of particles. Let x, y, z be the components of the velocity of each particle in three rectangular directions, and let the number of particles for which x lies between x and $x + dx$, be $Nf(x)dx$, where $f(x)$ is a function of x to be determined.

The number of particles for which y lies between y and $y + dy$ will be $Nf(y)dy$; and the number for which z lies between z and $z + dz$ will be $Nf(z)dz$, where f always stands for the same function.

Now the existence of the velocity x does not in any way affect that of the velocities y or z , since these are all at right angles to each other and independent, so that the number of particles whose velocity lies between x and $x + dx$, and also between y and $y + dy$, and also between z and $z + dz$, is

$$\underline{Nf(x)f(y)f(z)dx dy dz.}$$

But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is

$$\underline{f(x)f(y)f(z) = \phi(x^2 + y^2 + z^2)}.$$

Solving this functional equation, we find

g

$$\underline{f(x) = Ce^{Ax^2}}, \quad \underline{\phi(r^2) = C^3 e^{Ar^2}}.$$

If we make A positive, the number of particles will increase with the velocity, and we should find the whole number of particles infinite. We therefore make A negative and equal to $-1/\alpha^2$, so that the number between x and $x + dx$ is

$$\underline{NCe^{-(x^2/\alpha^2)} dx}.$$

Integrating from $x = -\infty$ to $x = +\infty$, we find the whole number of particles,

$$\underline{NC\sqrt{\pi}\alpha = N}, \quad \underline{\therefore C = \frac{1}{\alpha\sqrt{\pi}}},$$

$f(x)$ is therefore $\frac{1}{\alpha\sqrt{\pi}} e^{-(x^2/\alpha^2)}.$

Whence we may draw the following conclusions:—

1st. The number of particles whose velocity, resolved in a certain direction, lies between x and $x + dx$ is

$$N \frac{1}{\alpha\sqrt{\pi}} e^{-(x^2/\alpha^2)} dx. \quad (1)$$

2nd. The number whose actual velocity lies between v and $v + dv$ is

$$N \frac{4}{\alpha^3\sqrt{\pi}} v^2 e^{-(v^2/\alpha^2)} dv. \quad (2)$$

3rd. To find the mean value of v , add the velocities of all the particles together and divide by the number of particles; the result is

$$\text{mean velocity} = \frac{2\alpha}{\sqrt{\pi}}. \quad (3)$$

4th. To find the mean value of v^2 , add all the values together and divide by N ,

$$\text{mean value of } v^2 = \frac{3}{2}\alpha^2. \quad (4)$$

This is greater than the square of the mean velocity, as it ought to be.

$$P = \frac{1}{3} nm \overline{v^2}$$

$$= \frac{1}{3} nm \left(\frac{3}{2} \alpha^2 \right)$$

$$= \frac{1}{2} nm \alpha^2$$

$$P = nkT$$

$$\alpha^2 = \frac{2kT}{m}$$

$$\frac{dn(v_x, v_y, v_z)}{N} = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left[-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T} \right] dv_x dv_y dv_z$$

Further Studies on the Thermal Equilibrium of Gas Molecules *

(1872)

LUDWIG BOLTZMANN

SUMMARY

According to the mechanical theory of heat, the thermal properties of gases and other substances obey perfectly definite laws in spite of the fact that these substances are composed of large numbers of molecules in states of rapid irregular motion. The explanation of these properties must be based on probability theory, and for this purpose it is necessary to know the distribution function which determines the number of molecules in each state at every time. In order to determine this distribution function, $f(x, t)$ = number of molecules having energy x at time t , a partial differential equation for f is derived by considering how it changes during a small time interval as a result of collisions among molecules. If there are no external forces, and conditions are uniform throughout the gas, this equation takes the form (equation (16)):

$$\frac{\partial f(x, t)}{\partial t} = \int_0^\infty \int_0^{x+x'} \left[\frac{f(\xi, t)}{\sqrt{\xi}} \frac{f(x+x'-\xi, t)}{\sqrt{(x+x'-\xi)}} - \frac{f(x, t)}{\sqrt{x}} \frac{f(x', t)}{\sqrt{x'}} \right] \sqrt{(xx')} \psi(x, x', \xi) dx' d\xi$$

where the variables x and x' denote the energies of two molecules before a collision, and ξ and $(x+x'-\xi)$ denote their energies after the collision; $\psi(x, x', \xi)$ is a function which depends on the nature of the forces between the molecules.

If the velocity distribution is given by Maxwell's formula

$$f(x, t) = (\text{constant}) \sqrt{x} e^{-hx}$$

* [Originally published under the title "Weitere Studien über das Wärme-gleichgewicht unter Gasmolekülen", in *Sitzungsberichte Akad. Wiss.*, Vienna, part II, 66, 275-370 (1872); reprinted in Boltzmann's *Wissenschaftliche Abhandlungen*, Vol. I, Leipzig, J. A. Barth, 1909, pp. 316-402.]



For an isolated system: $\Delta S \geq 0$

On the Relation of a General Mechanical Theorem to the Second Law of Thermodynamics *

LUDWIG BOLTZMANN

(1877)

SUMMARY

Loschmidt has pointed out that according to the laws of mechanics, a system of particles interacting with any force law, which has gone through a sequence of states starting from some specified initial conditions, will go through the same sequence in reverse and return to its initial state if one reverses the velocities of all the particles. This fact seems to cast doubt on the possibility of giving a purely mechanical proof of the second law of thermodynamics, which asserts that for any such sequence of states the entropy must always increase.

Since the entropy would decrease as the system goes through this sequence in reverse, we see that the fact that entropy actually increases in all physical processes in our own world cannot be deduced solely from the nature of the forces acting between the particles, but must be a consequence of the initial conditions. Nevertheless, we do not have to assume a special type of initial condition in order to give a mechanical proof of the second law, if we are willing to accept a statistical viewpoint. While any individual non-uniform state (corresponding to low entropy) has the same probability as any individual uniform state (corresponding to high entropy), there are many more uniform states than non-uniform states. Consequently, if the initial state is chosen at random, the system is almost certain to evolve into a uniform state, and entropy is almost certain to increase.

* Originally published under the title: "Über die Beziehung eines allgemeinen mechanischen Satzes zum zweiten Hauptsatze der Warmetheorie", *Sitzungsberichte Akad. Wiss.*, Vienna, part II, 75, 67-73 (1877); reprinted in Boltzmann's *Wissenschaftliche Abhandlungen*, Vol. 2, Leipzig, J. A. Barth, 1909, pp. 116-22.]

Boltzmann (1898)

As the first part of the *Gas Theory* was being printed, I had already almost completed the present second and last part, in which the more difficult parts of the subject were not to have been treated. It was just at this time (1895) that attacks on the theory of gases began to increase. I am convinced that these attacks are merely based on a misunderstanding, and that the role of gas theory in science has not yet been played out.

In my opinion it would be a great tragedy for science if the theory of gases were temporarily thrown into oblivion(遺忘) because of a momentary hostile attitude toward it, as was for example the wave theory because of Newton's authority.

I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered.

The fundamental Postulate

All microstates of an isolated system are equally likely.

等几率假定

Macrostate	Possible microstates (H = heads, T = tails)	Number of microstates
4 heads	HHHH	1
3 heads, 1 tail	HHHT, HHTH, HTHH, THHH	4
2 heads, 2 tails	HHTT, HTHT, THHT, HTTH, THTH, TTHH	6
1 head, 3 tails	TTTH, TTHT, THTT, HTTT	4
4 tails	TTTT	1

TABLE 20–1 Probabilities of various macrostates for 100 coin tosses

Macrostate		Number of microstates W
Heads	Tails	
100	0	1
99	1	1.0×10^2
90	10	1.7×10^{13}
80	20	5.4×10^{20}
60	40	1.4×10^{28}
55	45	6.1×10^{28}
50	50	1.0×10^{29}
45	55	6.1×10^{28}
40	60	1.4×10^{28}
20	80	5.4×10^{20}
10	90	1.7×10^{13}
1	99	1.0×10^2
0	100	1

Entropy is a measure of the probability of a (macro)state and that the Second law reduces to stating that natural evolution is from improbable to more probable (macro)states.

$$S = k_B \ln W$$

等几率假定

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2 heads, 2 tails	HHTT, HTHT, THHT, HTTH, THTH, TTHH	6
1 head, 3 tails	TTTH, TTHT, THTT, HTTT	4
4 tails	TTTT	1

$$S = k_B \ln W$$

$$S = k \cdot \log W$$



LVDWIG
BOLTZMANN
1844-1906

HENRIETTE
BOLTZMANN
GEB. EDLE VON AIGENTLER
1854-1938

DR. PHIL. PAULA
BOLTZMANN

GEB. CHIARI
1891-1977

ARTHUR
BOLTZMANN
DIPL. ING. DR. PHIL. HOF RAT

1881-1952

LVDWIG
BOLTZMANN

1923-1943

LETZTER MÄNNLICHER NACHKOMME
GEFALLEN BEI SMOLENSK

信息与熵

1. 生于2000年的某一天, $W=365$

2. 生于2000年上半年, $W=182$

3. 生于2000年的3月, $W=31$

4. 生于2000年的3月22日, $W=1$

$$S = k_B \ln W$$

什么是信息？信息的概念既抽象又多变。信息既不是物质，也不是能量。

“组成我们的客观世界，有三大基本要素：除了物质和能量之外，还有信息”。

美国学者、哈佛大学的欧廷格（A. G. Oettinger）对这三大基本要素作了精辟的诠释：“没有物质什么都不存在，没有能量什么都不会发生，没有信息什么都没有任何意义”。

A. Einstein

“A theory is the more impressive the greater the simplicity of its ^{前提} premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made upon me; it is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, will never be overthrown.”
^{推翻}

课后阅读：

1. 热寂说疑案新论
2. 探究热力熵本源的研究历程