CHAPTER 1

THE STATISTICAL BASIS OF THERMODYNAMICS

IN THE annals of thermal physics, the fifties of the last century mark a very definite epoch. By that time the science of thermodynamics, which grew essentially out of an experimental study of the macroscopic behavior of physical systems, had become, through the work of Carnot, Joule, Clausius and Kelvin, a secure and stable discipline of physics. The theoretical conclusions following from the first two laws of thermodynamics were found to be in very good agreement with the corresponding experimental results.[1] At the same time, the kinetic theory of gases, which aimed at explaining the macroscopic behavior of gaseous systems in terms of the motion of the molecules and had so far thrived more on speculation than calculation, began to emerge as a real, mathematical theory. Its initial successes were glaring; however, a real contact with thermodynamics could not be made until about 1872 when Boltzmann developed his *H*-theorem and thereby established a direct connection between entropy on one hand and molecular dynamics on the other. Almost simultaneously, the conventional (kinetic) theory began giving way to its more sophisticated successor–the ensemble theory. The power of the techniques that finally emerged reduced thermodynamics to the status of an "essential" consequence of the get-together of the *statistics* and the *mechanics* of the molecules constituting a given physical system. It was then natural to give the resulting formalism the name *Statistical Mechanics*.

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قوانین ترمودینامیک

قانون صفرم :

اگر جسم A با جسم B و جسم B با جسم C در حال تعادل باشد جسم A با جسم C نیز در حال تعادل است . این قانون عملاً کمیت دما را تعریف می کند .

قانون اول :

قانون بقای انرژی است و انرژی درونی را معرفی می کند که یک دیفرانسیل کامل است .

$$dU = dQ - dW$$

$$dU = dQ - PdV + H.dM + E.dP + \sum_j \mu_j dN_j + \sigma.dA + J.dl + \varphi d\varepsilon$$

قانون دوم :

آنتروپی را تعریف می کند .

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

قانون سوم :

با تعداد گام های باز گشت پذیر بین دو سیستم نمی توان ΔS را به سمت صفر برد مگر اینکه $T \to 0$. رسیدن به دمای صفر مطلق کلوین غیر ممکن است .

ترکیب قانون اول و قانون دوم:

$$dU \leq TdS - PdV + H.dM + E.dP + \sum_j \mu_j dN_j + \sigma.dA + J.dl + \varphi d\varepsilon$$

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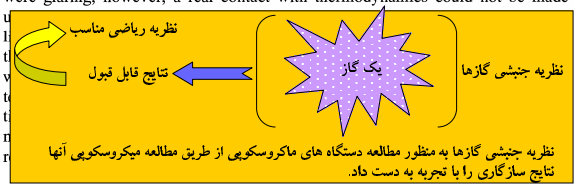

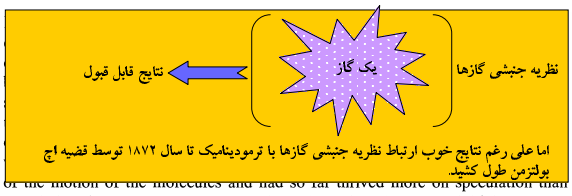

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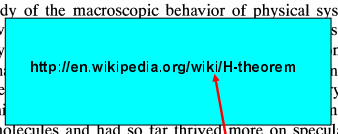

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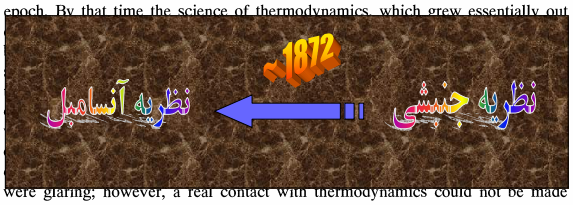

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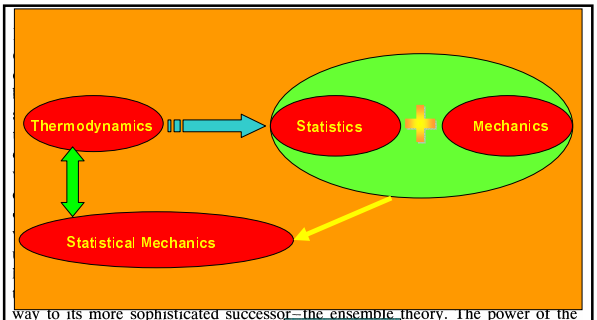

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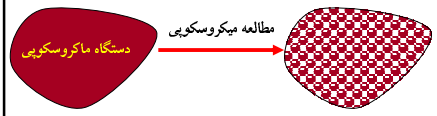
As a preparation towards the development of the formal theory, we start with a few general considerations regarding the statistical nature of a macroscopic system. These considerations will provide ground for a statistical interpretation of thermodynamics. It may be mentioned here that, unless a statement is made to the contrary, the system under study is supposed to be in one of its equilibrium states.



1.1. The macroscopic and the microscopic states

We consider a physical system composed of N identical particles confined to a space of volume V. In a typical case, N would be an extremely large number—generally, of order 10^{23}. In view of this, it is customary to carry out analysis in the so-called *thermodynamic limit*, viz. $N \to \infty$, $V \to \infty$ (such that the ratio N/V, which represents the *particle density* n, stays fixed at a preassigned value). In this limit, the *extensive* properties of the system become directly proportional to the size of the system (i.e. proportional to N or to V), while the *intensive* properties become independent thereof; the particle density, of course, remains an important parameter for all physical properties of the system.

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کمیت های فزو نور v x و نافزو نور v

پارامترهایی که یک حالت ترمودینامیکی را به طور کامل معیین می کنند متغییرهای حالت نام دارند.
متغییرهای حالت دو نوع اند: ۱) متغییرهای حالت فزونور ۲) متغییرهای حالت نافزونور

کمیت فزونور به صورت زیر تعریف می شود که بیانگر یک تابع همگن مرتبه اول از متغییرهای اکسنسیو حالت دستگاه است.

If S is extensive, then $S(\lambda N, \lambda V, \lambda E) = \lambda S(N, V, E)$

یعنی اگر متغییرهای فزونور حالت را با ضریب λ افزایش (کاهش) دهیم، آنگاه آن کمیت نیز با ضریب λ افزایش (کاهش) می یابد.

بنابراین اگر دستگاهی متشکل از زیر دستگاه های کوچکتر داشته باشیم، آنگاه می توان گفت که کمیت فزونور آن دستگاه برابر با مجموع همان کمیت فزونور زیر دستگاه های تشکیل دهنده آن است.

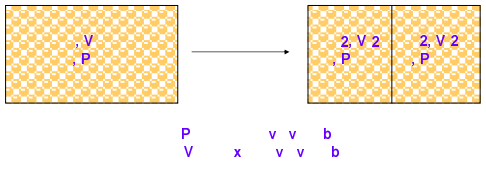
If $S(\lambda N, \lambda V, \lambda E) \neq \lambda S(N, V, E)$, then S is intensive.

انواع کمیت های فزو نور extensive و نافزو نور intensive

متغییرهای فزونور و نافزونور اغلب به صورت جفتی ظاهر می شوند. آنها با نیروهای تعمیم یافته و جابجاییهای تعمیم یافته متناظرند .

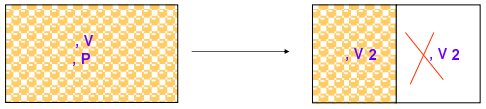
dW ⟶ F dX , PdV ..... đdq

مختصه ی فزو نور		مختصه ی نافزو نور		سیستم های ساده
V	حجم	P	فشار	سیستم هیدروستاتیکی
L	طول	J	کشش	سیم کشیده
A	مساحت	σ	کشش سطحی	فیلم سطحی
Z	بار	ε	نیروی الکترومونوری	باتری الکریکی
P	قطبش	E	شدت الکتریکی	بر، ی دی الکتریک
M	آهنربایش	H	شدت مغناطیسی	میله ی پارامغناطیس



P v v b
V x v v b

دقت شود که باید هم تعداد درجات آزادی و هم اندازه هردو نصف شوند. مثلا حالت زیر قابل قبول نیست:



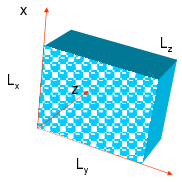
Next we consider the total energy E of the system. If the particles comprising the system could be regarded as non-interacting, the total energy E would be equal to the sum of the energies ε_i of the individual particles:

$$E = \sum_i n_i \varepsilon_i, \qquad (1)$$

where n_i denotes the number of particles each with energy ε_i. Clearly,

$$N = \sum_i n_i. \qquad (2)$$

تمرین: رابطه (۱) را اثبات کنید. راهنمایی:



$$V(\vec{X}) = \begin{cases} 0 & \text{داخل جعبه} \\ \infty & \text{خارج و روی دیواره ها} \end{cases}$$

According to quantum mechanics, the single-particle energies ε_i are discrete and their values depend crucially on the volume V to which the particles are confined. Accordingly, the possible values of the total energy E are also discrete. However, for large V, the spacing of the different energy values is so small in comparison with the total energy of the system that the parameter E might well be regarded as a *continuous* variable. This would be true even if the particles were mutually interacting; of course, in that case the total energy E cannot be written in the form (1).

$$\varepsilon = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2}{2m}\left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2\right]$$

$$L_x = L_y = L_z = L$$
$$n_x = n_y = n_z = n$$
$$L^3 = V \Rightarrow L = V^{1/3}$$

$$\Rightarrow \quad \varepsilon = \frac{\hbar^2 n^2}{2mL^2} \frac{\hbar^2 n^2}{2m V^{\frac{2}{3}}}$$

$$\varepsilon \propto V^{-2/3}$$

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ε_i are discrete $\Rightarrow$ $E = \sum_{i=1} n_i \varepsilon_i$ are discrete

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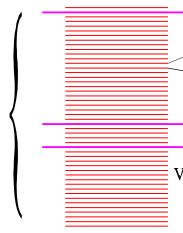

$E \gg \delta E$
$\delta E \gg \Delta$
$E \gg \Delta$

$\varepsilon_i \propto V^{-2/3} \Rightarrow V \Rightarrow \varepsilon_i$

V is large and ε_i is small but $N \sim 10^{23} \Rightarrow E = \sum_{i=1} n_i \varepsilon_i \gg \varepsilon_i$

$\Rightarrow$ E can be regarded as continuous variables

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If $V \neq 0$, then the particles are interacting. In this case: $E = \sum_{i=1} n_i \varepsilon_i$

اما با این وجود هنوز هم می توان گفت که انرژی E گسسته است (اگر چه میزان گسستگی آن به دلیل تبدیل شدن به نوار به جای تراز ناشی از برهمکنشها کمتر شده است). چون استدلال فوق در مورد حجم بزرگ جعبه و در پی آن کوچکی فاصله بین ترازها و بزرگ بودن E به دلیل بزرگ بودن N صادق است پس بازهم می توان انرژی را در مقیاسه با فاصله بین ترازها پیوسته فرض کرد.

خلاصه این که می توان E را یک کمیت ماکروسکوپی فرض کرد.

The specification of the actual values of the parameters N, V and E then defines a *macrostate* of the given system.

(N, V, E) یک حالت ماکروسکوپی

قبلا گفتیم که N و E کمیتهای ماکروسکوپی هستند. V نیز به طور طبیعی یک کمیت ماکروسکوپی است. پس سه کمیت N, V, E یک حالت ماکروسکوپی را برای یک دستگاه هیدرئ استاتیکی معین می کند، زیرا:

$$\begin{cases} dE = dQ - dw = dQ + pdV \\ dS \geq \dfrac{dQ}{T} \end{cases}$$

معادلات ماکسول

& با داشتن N, V, E

کلیه خواص ترمودینامیکی یک دستگاه ماکروسکوپی معین می شود:

تمرین ۲: معادلات ماکسول را به دست آورید (مرجع کتاب Reichl)