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Understanding structural stability and process spontaneity based on the rejection of the Gibbs paradox of entropy of mixing[1]

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Abstract

Logarithmic relations of entropy and symmetry and a linear relation of entropy and similarity were set up and have been used to predict the miscibility of fluids, the stability of solid structures, particularly molecular assemblages, and the electronic structures of atoms and molecules. After the rejection of the Gibbs paradox statement of mixing, it becomes clear mixing most similar or indistinguishable components (such as individual subphases, quantum states) and any analogous processes are the most spontaneous processes. Therefore, entropy as information loss can be defined and quantified for dynamic and static structures at a hierarchical level. Entropy changes can be estimated for many symmetry-breaking processes such as crystallization and ferromagnetism. Accordingly, the informational temperature of a conventional molecular assemblage in the solid state, and the local thermodynamic temperature of electronic motion, can be formally defined and have been found to be negative temperatures. The most spontaneous process of mixing most similar or indistinguishable components can be regarded as the deformation of a flexible system, e.g. an ideal fluid body and the deformation can deliver mechanical work. © 1997 Elsevier Science B.V.

Keywords: Gibbs paradox; Information theory; Symmetry breaking; Similarity index; Negative temperature; Shape evolution

1. Introduction

The Gibbs paradox statement [1–15] has been a very fundamental assumption in statistical mechanics [1,14]. It says that the entropy of mixing or assembling to form solid assemblages, liquid and gas mixtures or any other analogous assemblages such as quantum states, *decreases discontinuously* with the increase in the property similarity of the composing individuals [4,14,15]. Some authors revised the Gibbs paradox statement and argue that the entropy of mixing decreases continuously with the increase in the property similarity of the composing individuals [6,8,10,16]. Based on a large body of experimental evidence and theoretical arguments [1–3], this statement was disproved and a new theory built up which says that entropy of mixing or assembling *increases continuously* with the increase in similarity (Fig. 1).

Further developments and applications of this new theory [17–20] are outlined in the present paper.

Based on the second law of thermodynamics, the entropy (S) increase used to predict the structural stability and the process spontaneity of a system of ideal gas used in a Carnot heat engine can be directly measured as a maximum mechanical work. Because

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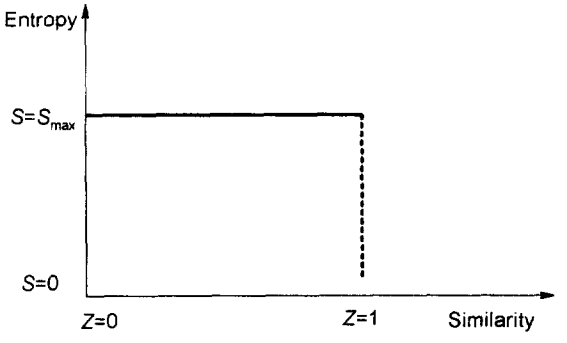
(a) J. W. Gibbs: *Decrease discontinuously*



(b) The present author: *Increase continuously*

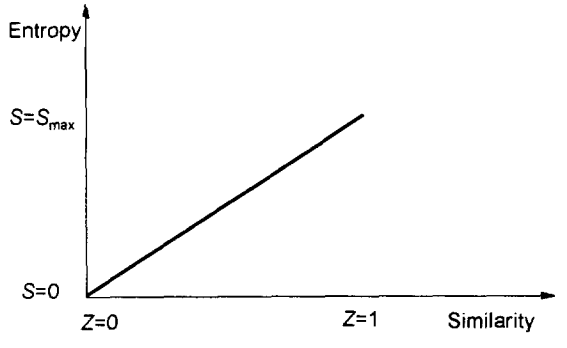


Fig. 1. Correlation of the entropy of mixing with similarity according to (a) conventional statistical physics where the entropy of mixing suddenly becomes zero if the components are indistinguishable [4–14], and (b) the theory of the present author [1–3].

mixing of ideal gases is a process of entropy increase, in principle, a maximum mechanical work

$$w = \Delta G = -T\Delta S \tag{1}$$

should be also measurable, where G is the Gibbs free energy and T is temperature. A balloon model will be used to realize the mechanical work output of the isobaric, isothermal and isochoric energy transduction. After the rejection of the Gibbs paradox statement of mixing, the most spontaneous process of mixing most similar or indistinguishable components can be regarded as the deformation of an ideal fluid body within an enclosure (Section 5).

However, because the entropy of mixing ideal gases by simply opening the walls separating rigid containers has no observable effects such as heat and mechanical work, it is desirable to consider entropy generally as information loss. Therefore, entropy should be generally correlated to other much more conceivable properties such as symmetry (higher symmetry is correlated with higher entropy [1]) and similarity (Section 2 and Ref. [17]). This gives a very general expression of the second law of thermodynamics. It is found that indistinguishability is a ubiquitous driving force for many physical and chemical processes.

It is convenient to consider a hierarchical level of nature and to consider locally both the dynamic and static aspects at a hierarchical level. Two temperatures are formally defined for the dynamic and static aspects; some local temperatures have values that are normally negative. An entropy and information theory is developed based on the rejection of the Gibbs paradox statement and is found to conform perfectly with the second law of thermodynamics and to predict structural stability and process spontaneity of symmetry-breaking processes such as second-order phase transition phenomena (Section 3 and Ref. [18]). There is no reason to infuse mystery into the formation of a static (such as crystallization) or a dynamic pattern (such as chemical oscillation[2]).

According to Heisenberg [22], von Neumann [16] and Pauling [23], the chemical bond can be characterised by a mixing of quantum states. The structural stability and process spontaneity of an electronic system in atoms and molecules can be investigated based on the new entropy theory of mixing (Section 4). Pauling's resonance theory is clearly justified by connecting it with the second law of thermodynamics through our new theory [19].

2. Mixing and separation [17]

From the general expression of entropy (k is a positive constant),

$$S = -k \sum_{i=1}^{w} \rho_i \ln \rho_i \tag{2}$$

[2] For an earlier critique of Prigogine's school of thermodynamics and his theory of structural stability and process spontaneity, see Ref. [21].

with

$$\sum_{i=1}^{w} \rho_i = 1 \tag{3}$$

and the well-known inequality [1]

$$-\sum_{i=1}^{w} \rho_i \ln P_i \leq \ln w \tag{4}$$

the entropy of mixing w subsystems increases continuously and monotonously with the property similarities of the subsystems; the property indistinguishability corresponds to the maximal entropy of mixing (Fig. 1):

$$S_{max} = k \ln w \tag{5}$$

The values ρ_i in Eq. (2) are determined by the pairwise similarity comparison of *any* relevant properties among the w subsystems to be mixed. The first kind of such properties are such obvious physical properties as volume fractions, partial pressures or molar fractions. The other kind of property can be generally named as molecular similarity, a physicochemical property [24].

Obviously, indistinguishability is a ubiquitous driving force for physical and chemical processes, because it is related to the highest symmetry and entropy characteristic of a global equilibrium [1]. The logarithmic relations of entropy and symmetry provided a very sound basis for a general theory of structural stability and process spontaneity according to symmetry evolution consideration [1]. Note that the Greek word symmetry means *same measure* or the measure of sameness, or the measure of indistinguishability.

This theory conforms with all the practically useful entropy formulae hitherto established for the first category of property similarities among subsystems. For example, relative to the state before mixing, the entropy of mixing ideal gases and ideal solutions is:

$$S = -nR \sum_{i=1}^{w} x_i \ln x_i \tag{6}$$

after mixing of w components of molar fractions x_i, with the total mole number n. The entropy of mixing is S_{max} only if x_i all have identical values.

This theory also conforms well with all those related experimental observations that may contradict conventional statistical mechanics for molecular similarity consideration (Fig. 1(a)). An example is the hydrophobic effect. Hydrophobicity is a property of organic molecules closely related to molecular similarity [24]. Hydrophobic subsystems of pentane and hexane are mutually miscible and form a separated phase in water because they have similar properties. Subsystems of identical hydrocarbons merge very spontaneously because they are very similar or indistinguishable (note that the entropy effect dominates over the hydrophobic effect [25]).

By using some simple model molecular systems having several energy levels [26], it has been shown that entropy, similarity and thus general miscibility, all increase with the increase in temperature of the subsystems [17]. At reduced temperatures, where the similarity is reduced [26], different substances do not mix but separate as a result of the fact that *the indistinguishable subsystems are the most miscible ones, whether they are solids liquids, or gases.* A straightforward organic preparation procedure has thus been designed and demonstrated by both synthesis and purification of several quinoxaline-2,3-diones in one step [27].

A similarity index is defined as the ratio of the entropy and the maximal entropy:

$$Z = S/S_{max} \tag{7}$$

corresponding to the maximal similarity ($Z = 1$, i.e. indistinguishability), as shown in Fig. 1(b). Succinctly, if one wants to mix substances, one should increase the similarity (of relevant properties); if one plans to separate the substances as phases, one should reduce the similarity. The desirable processes of mixing or separation will then happen spontaneously.

3. Self-organization in hierarchical structures [18]

Self-organization is a spontaneous process and must be governed generally by the second law of thermodynamics. However, dissipative structure theory defines "order out of chaos" through "self-organization" and means that a more "ordered" state is generated through a spontaneous process. This has been used as an example against the validity of the second law of thermodynamics [28,29]. Therefore, we need to construct a new informational theoretical and thermodynamic explanation.

Firstly, in order to make any meaningful discussion possible, entropy (S) is defined as the information (I) loss:

$$S = I_{max} - I \tag{8}$$

where I_{max} is the maximum information presumably registerable. This is necessary because in some definitions [30], entropy and information are regarded as the same parameter.

More generally, conventional information theory defines the total amount of information (I) registered by a system as the difference between the system's actual entropy (S) and its maximum entropy (S_{max}),

$$I = S_{max} - S \tag{9}$$

In a process, if all the information is lost relative to the initial state ($I = I_{max}$), according to Eq. (9) the final state has maximum entropy

$$S_{max} = \ln w \tag{10}$$

where the positive constant k is defined as 1 and w is the number of indistinguishable "microstates" (or, in some cases, the number of the arrangements, or combinations) [30]. Again, it is well known that the increase in entropy is synonymous with the loss of information. Clearly,

$$I_{max} = S_{max} \tag{11}$$

which means that the maximum information a system can lose equals the maximum information the system may register. It is necessary to state that both entropy and information are non-negative functions:

$$S \geq 0 \tag{12}$$

$$I \geq 0 \tag{13}$$

Furthermore, it is very convenient that a local thermodynamic model be set up for the consideration of the structural stability and process spontaneity of a hierarchical level, and the energy E_ℓ, and entropy S_ℓ are defined for that hierarchical level. Temperatures T_ℓ, which connects energy E_ℓ and entropy S_ℓ, can be defined (at least formally) for different structures of a hierarchical level:

$$\left(\frac{\partial E_\ell}{\partial S_\ell}\right)_{V_\ell} = T_\ell \tag{14}$$

It is not surprising that at some hierarchical level, the temperatures T_ℓ thus defined will be negative if the entropy increases while the energy decreases [31,32]. Because the change in E_ℓ can be measured, T_ℓ will be significantly, at least formally, defined, and in principle easily calculated, if the change of S_ℓ as information loss, which will be discussed in the following, can be calculated.

Two general mechanisms of information loss in any hierarchical level are proposed: information loss happens because of the *dynamic* motion or the formation of a more symmetrical *static* structure. Therefore, for a hierarchical level, a thermodynamic temperature T (for its dynamic aspect) and an informational temperature T_I (for its static aspect; so called because in practice information is registered on a *static* solid device) can be defined respectively.

For conventional thermodynamic systems of many particles (molecules), the thermodynamic temperature T is conventionally defined as positive (non-negative). For such systems, because information registration is a process of $\Delta I > 0$, or $\Delta S < 0$, and involves the energetically excited states ($\Delta E > 0$) [33], T_I in a conventional thermodynamic system at static state is always negative [31]. When the system is in a fluid state, the negative information temperature is at its maximum value: $T_I = 0$.

For a hierarchical level of a single atom and a molecule, the electronic system has a negative local thermodynamic temperature T of electron motion and a positive local informational temperature T_I relative to the thermodynamic temperature of the conventional thermodynamic system of an ideal gas [32]. For electronic motions, locally the total energy E_e and the entropy S_e vary in such a way that E_e reduces while S_e increases. The local thermodynamic temperature T is negative if Eq. (14) is used. The kinetic energy K_e of electronic motion can be calculated from the virial theorem: K_e increases with the decrease in the total energy E_e. Locally both K_e and S_e increase with the increase of the absolute value of the local thermodynamic temperature, $|T_e|$, or when T_e becomes more negative and when the system approaches the ground state [32].

Because it is allowed to evolve spontaneously, the more *self*-organized system will be closer to an equilibrium structure (either dynamic or static). Because a system closer to equilibrium has a higher entropy [34], "order out of chaos" through "self-organization" must be false, whether or not it is at

equilibrium. This is obvious for a dynamic system. For the comparison of the relative stabilities of different static structures, let us take crystallization as an example. Crystallization has been taken as a typical example of self-organization [35].

We introduced a formula

$$I = N \ln M_a \tag{15}$$

to calculate the values of information of different static structures based on the estimation of the apparent species number (M_a) factually observed in a system of N molecules [36]. For example if M molecular orientations are originally used to register information in an assemblage of many molecules in the solid state, then, comparing with the imperfect crystal of M species (M orientations), there is factually only one orientation, or one species ($M_a = 1$) observed in a perfect crystal, and the information is completely lost:

$$I = \ln 1 = 0 \tag{16}$$

From Eq. (8), relatively this is a state of maximum informational entropy.

Any system with large amount of information registered can be neither crystal-like nor very symmetric. One can claim to understand the structure of all 6.022×10^{23} cells in 1 mole of perfect crystal if one acquires information about only one of them. One cannot say this if the solid is not a perfect crystal. Regarding a perfect crystal as "order" and an imperfect crystal as "disorder" and using the theory of "order out of chaos" through "self-organization" will naturally lead either to the conclusion that a static structure of a perfect crystal is generally less stable than an amorphous static structure, which is against the fact that crystals are the most stable static structures, or to the conclusion that entropy decreases (information increases) spontaneously in an information registration system (that can be an isolated system), which is then against the second law of thermodynamics. The opposite is correct.

Of course, construction of this new theory of structural stability is possible only if the Gibbs paradox statement is rejected. Remember that the Gibbs paradox expression of entropy has also been applied to static assemblages such as spin and molecular orientation (see any treatment of statistical mechanics in the solid state [37]). The present new theory says that the formation of a perfect crystal, relative to imperfect crystals, has more information loss, and is more stable. Unfortunately, none of the many relevant entropy theories of the Ising model [37] built so far is correct, because they are based on the Gibbs paradox statement. The related interesting topic of chemical aesthetics can be discussed with many examples: symmetry is ugly because it is associated with information loss [38].

Clearly, for symmetry breaking problems in solid state physics, entropy changes can be estimated as the amounts of information loss for many processes such as crystallization (molecular orientations) and ferromagnetism (spin orientations). Factually all the other symmetry breaking phenomena observed in nature, such as phase transformation and phase separation, can all be elegantly explained by this new theory in an analogous way.

Finally, the total entropy $S_{\ell tot}$ of a system at the hierarchical level ℓ can be expressed as the sum of the thermodynamic entropy (S_ℓ) and the informational entropy ($S_{\ell I}$) of the dynamic and static aspects:

$$S_{\ell tot} = S_\ell + S_{\ell I} \tag{17}$$

Then the total entropy of a structure with many hierarchical levels can be calculated and the entropy change during a self-organization can in principle be calculated.

4. Formation of the chemical bond [19]

Is there a reliable criterion for the structural stability and process spontaneity of an electronic system in atoms and molecules? With this question we return to Pauling's authentic work *The Nature of the Chemical Bond*, in which we find a most important keyword – resonance [23]. The most prominent effect of resonance (mixing of quantum states), as illustrated by Pauling with numerous examples, is observed if it occurs among several energetically indistinguishable configurations (e.g. $H^+ \cdot H$ and $H \cdot {}^+H$ for the formation of a one-electron bond in H_2^+). Pauling specifically and most frequently used benzene (C_6H_6) to explicitly illustrate the nature of resonance and the significance of the π-electron delocalization. However, it is this interpretation of benzene's structural stability that continues to arouse controversy, as reviewed recently [39].

The use of entropy change as a criterion was considered a long time ago [16]. In his well-known quantum mechanical resolution of the Gibbs paradox statement of entropy of mixing, von Neumann provided a formula for the entropy of mixing of quantum states: mixing indistinguishable quantum states gives zero entropy while mixing different quantum states gives a nonzero value [16]. Because his mathematical manipulation of entropy of the electronic system was strictly restricted to the framework of the Gibbs paradox statement, and the Gibbs paradox statement itself is false (see the previous sections of this paper), it is understandable that his entropy of mixing formula [16] has virtually never been applicable to an electronic system even though it was originally expected to serve as a process spontaneity criterion of electronic systems of single atoms and molecules (see also Ref. [10]).

Firstly, because electrons involved in chemical bond formation are of one type of particle, it is expected that a limited amount of entropy increase of the mixing of the indistinguishable particles, here the electrons, results in a chemical bonding process.

Secondly, the electronic configurations of the ground state and the bonding orbital are always more symmetric than those of excited states and anti-bonding orbitals. From the logarithmic relation of entropy and symmetry (higher entropy correlates with higher symmetry) [1], the formation of the more stable ground state and the chemical bond is a process of entropy increase.

Thirdly, all the quantum mechanics calculations (either simple ones like both VB and MO theories or many dedicated methods) and experimental facts [2] unambiguously show, opposing von Neumann's conclusion [10,16], that the mixing of quantum states that are indistinguishable in properties (energy and/or configuration) gives the maximum entropy and leads to the most stable state. Several very useful, although very simple, principles, such as the maximum overlapping principle, resonance theory and some other empirical rules, can be immediately justified, based on a general criterion of indistinguishability and maximum entropy for quantum mechanical systems. For instance, we may apply the term "mixing" as used by von Neumann to a quantum system [10,16]: resonance among several energetically and configurationally indistinguishable structures, such as the Kekule structures of benzene, is the most prominent.

5. Deformation in energy transduction [20]

Life is restricted to a very narrow range of environmental conditions, particularly of pressure and temperature, in the biosphere (for a human body, they are 1 atm and 37°C). This is fundamentally different from a heat engine which converts chemical energy to expansion work over a large range of pressure (P), temperature (T) and volume (V) changes in processes such as a Carnot cycle. There must be a very different mechanism governing the very efficient *isobaric, isothermal* and *isochoric* energy transduction in the physiological processes of muscle relaxation and the contraction cycle. Unfortunately so far we still lack a clear satisfactory model of bioenergy transduction in muscle contraction and relaxation cycles [40], even though we already know many details at the molecular level such as ATP chemical thermodynamics.

A fluid body is confined within an interface, such as fluid in a cell, and gas in a balloon. Fluid body deformation has been treated thoroughly by Gibbs as an interfacial phenomenon (for example, the interface of hydrophobic fluid and water), and this treatment has been only slightly modified so far [41]. However, it has been repeatedly observed that a fluid body within a flexible interface spontaneously assumes the most symmetric, i.e. spherical, shape, at equilibrium. This suggests that the deformation of a fluid body itself is an energy transduction mechanism.

Consider a model of an ideal gas in a balloon. An *isobaric, isothermal* and *isochoric* process can be characterized by a free energy increment $\Delta G = -T\Delta S$ if $\Delta H = 0$. Mixing (or the combination) of indistinguishable gases, which we believe to have an entropy increase (see Section 2), may be regarded as a deformation. This is illustrated by change of the N smaller enclosures of identical shapes to a final total volume

$$V = \sum_{i=1}^{N} V_i \tag{18}$$

of the same shape to give

$$\Delta S = k \sum_{i=1}^{N} N_i \ln (V/V_i) \tag{19}$$

More general deformation is a very complicated problem of differential geometry and will be discussed elsewhere. If carried out reversibly, from Eq. (1), this step will perform nonexpansion mechanical work in the quantity of $-\Delta G = T\Delta S$, with ΔS as calculated. For example, we predict that the deformation of an ideal gas in a balloon from a shape of two identical spheres (each of $0.5V$) to a final single sphere of volume V can perform a mechanical work as much as that of an isothermal expansion from a volume of $0.5V$ to a final volume V.

In conclusion, Gibbs' statement that the "deformation of a fluid is immaterial" [42], is incorrect. We say that deformation is a process with information change and entropy change, and in some cases with energy change, which can be estimated after the rejection of the Gibbs paradox statement. It has been noticed that the deformation is also a process of symmetry evolution [1]. For example, protein folding is a process of shape evolution from an odd-shaped macromolecule to the most symmetric spherical shape.

Like the Carnot cycle, the working substance in the balloon model is also an ideal gas. However, from the general expression for the deformation, ΔS is related to the area as well as the curvature of the flexible interface enclosing the working gas. It may be proposed that, analogously, by consuming chemical energy, flexible proteins unfold and separate in a muscle relaxation step. Muscle contraction is a step of protein folding and protein combination to perform mechanical work.

We noticed earlier that by simply opening the door connecting two rigid chambers of gases we cannot have any observable mechanical work output, whether the gases are identical or different. It is understandable that this problem is a pure information theoretical problem. More specifically it is a problem of defining the positive constant k in Eq. (2) and other equations used by Shannon, who only stated that k is a positive constant in his information theory [43], and its relation to the Boltzmann constant k_B, which is the thermodynamically significant constant. From this example of mixing of ideal gases, one should not simply state that the k used in information theory and the constant k_B used in thermodynamics and statistical physics are identical constants without more careful investigation. In some cases their relation can be easily found, e.g. Eqs. (2) and (6). However, in many other specific cases this problem is still open.

6. Discussion

6.1. Mixing of ideal gases

The main idea of the new theory [1–3], which has been demonstrated here to be broadly useful, is merely a direct consequence of the rejection of the Gibbs paradox. It is worthwhile to go back to the very original Gibbs paradox problem itself again: Suppose gases A and B in two rigid chambers are different gases. When the wall is removed, mixing of A and B happens because the particles diffuse into the larger space of the combined volume of both A and B.

When the wall dividing A and B is open, the two different sets of particles diffuse spontaneously, as commented by Gibbs himself [15]. Then a question follows: Is there anyone who can say that the particles in the case of the two chambers of identical gases *do not spontaneously* diffuse in a larger and combined space?

The answer is that the identical gases do spontaneously diffuse in the combined, larger space. Strictly speaking there is no such thing as different ideal gases. Once different *real* gases (nitrogen and oxygen) have been modeled and regarded as an ideal gas, the real gases should be taken as the same *ideal* gas, because there is only *one* definition of ideal gas. (It is logically wrong first to idealize all the real gases as one kind of ideal gas, and then to go back to handle them as different ideal gases.) Then the treatment of mixing ideal gases should be mathematically the same whether the gases are originally virtually different (nitrogen or oxygen) or virtually the same (both are air parts). In conclusion, Eq. (6) will be suitable for all cases of mixing *ideal* gases.

6.2. Information loss and information theory

Statistical mechanics has been regarded as the foundation of thermodynamics (see the subtitle of Gibbs' book [4]). Information theory is regarded as the foundation of statistical mechanics [44]. Therefore, information theory, particularly the concept of

information loss defined as entropy (S), should be expected to be applicable for predicting structural stability and process spontaneity of thermodynamic systems.

However, it has been a surprise that information theory has never been *practically* applied to thermodynamic or statistical mechanics problems so far. Only the opposite is true: thermodynamic concept of entropy (information loss) has been practically applied as the most important concept in information theory. The Gibbs–von Neumann relation (Eq. (2)) was introduced into information theory as the most important expression and useful for communication problems [43]. Another familiar statistical mechanics expression, the relation of entropy and the partition function (Q),

$$S = k \ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right)_V \tag{20}$$

was also adapted for information theory [44,45], which has been developed into a practically useful method only for data reduction of pure information manipulation.

Only after careful investigation was it finally realized that only if the Gibbs paradox statement (entropy of mixing *decreases discontinuously* with the similarity [Fig. 1(a)], or its revised version) is abandoned [1–3], is it possible to change this situation and to make the information theory concept of information loss applicable to the thermodynamic problems of structural stability and process spontaneity.

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