# Possible Decrease of Entropy due to Internal Interactions in Isolated Systems

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*If interactions and fluctuations exist among various subsystems of an isolated system, the entropy may not be an additive quantity. The second law of thermodynamics is based on statistical independence, etc. When these prerequisites do not hold, self-organized structures whose entropy is smaller may be formed. The possible decrease of entropy in an isolated system is discussed for plasma and evolutionary process of stars and the nonlinear interactions, etc.*

## 1. Introduction

The heat death of the Universe, which was unpalatable to Nernst (Browne 1995), is the most controversial question for thermodynamics. It has to be clearly pointed out that the entropy for an isolated system tends to a maximum, and the free energy or free enthalpy for a constrained system tends to a minimum. But, the development of the second law of the thermodynamics was usually based on an open system, for example, dissipative structure theory, synergetics, etc. (Davies et al. l986; Brandenberger et al. 1992; de Oliveira et al. 1992). The subadditivity of composite systems and extended thermodynamics have also been discussed (Wehrl 1978; Raggio 1995). Fort and Llebot (1995) proved that the classical entropy does not increase monotonically for an isolated fluid, therefore they considered that the generalized entropy of extended irreversible thermodynamics is more suitable for this fluid. Haken (1977) noted that for thermodynamics, in closed systems the entropy never decreases. The proof of this theorem is left to statistical mechanics.

To be quite frank, in spite of considerable effort this problem is not completely solved. The basis of thermodynamics is statistics, one of whose basic principles is statistical independence: The state of one subsystem does not affect the probabilities of various states of the other subsystems, because different subsystems may be regarded as weakly interacting (Landau *et al.* f980). This leaves the interactions among these subsystems out of consideration. But, if various internal complex mechanisms and interactions cannot be neglected, perhaps a self-organized structure may appear in an isolated system. In this case, the statistics and the second law of thermodynamics are possibly different. For instance, the entropy of an isolated fluid whose evolution depends on viscous pressure and the internal friction does not increase monotonically (Fort *et al.* 1995). When interactions exist among subsystems in an isolated system, the internal energy and the entropy are not additive extensive quantities (Chang 1994). They are dependent on structure: for example, the entropy of coherent light is not additive. In this case, statistical independence and equal-probability are unavailable. The additivity of entropy is postulated in statistical physics (Landau *et al.* 1980), but interactions among subsystems are neglected.

## 2. Some examples

Almost all matter in interstellar space can be considered to be a plasma, an ionized gas consisting of electrons, ions, and neutral atoms or molecules (Lang 1974). The pressure $P$ of a nondegenerate gas is

$$P = N_{tot}\frac{kT}{V} = r\frac{kT}{m}. \qquad (1)$$

For the gas the entropy is

$$S = kN_{tot}\ln\left[\frac{C(kT)^4}{P}\right] = kN_{tot}\ln\left[CP^3\left(\frac{m}{r}\right)^4\right]. \qquad (2)$$

In an isolated system, $N_{tot}$ is invariant,

$$S - S_o = kN_{tot}\ln\left[\left(\frac{P}{P_o}\right)^3\left(\frac{r_o}{r}\right)^4\right]. \qquad (3)$$

For a plasma,

$$P = N_{tot}(1+a)\frac{kT}{V} = (1+a)\frac{kTr}{m}, \qquad (4)$$

where $a = N_e/N_{tot}$ is the ionicity.

$$S - S_o = 3kN_{tot}\ln\left[\left(\frac{T}{T_o}\right)\left(\frac{r_o}{r}\right)^{g-1}\frac{1+a}{1+a_o}\right]. \qquad (5)$$

Here the entropy of the plasma is

$$S - S_o = c\ln\left[\left(\frac{T}{T_o}\right)\left(\frac{r_o}{r}\right)^{g-1}\frac{1+a}{1+a_o}\right], \qquad (6)$$

where $g = c_p/c_v$. In an isolated system of plasma, the ions will attract the electrons to neutral atoms. Since the plasma is often taken to be in local thermodynamic equilibrium (Lang 1974), and the total mass of an isolated system is constant, temperature $T$ and average density $r$ are invariant. Therefore, the final ionicity becomes smaller, so that the final entropy decreases.

For a mixture of gases, the increased entropy is

$$dS = -\sum_{j=1}^{m} n_j R\ln x_j . \qquad (7)$$

If the interactions of two mixed gases cannot be neglected, the change of Helmholtz s free energy will be (Reichl 1980)

$$F_j - F_i = RT[x_1\ln x_1 + x_2\ln x_2] + l\, x_1 x_2 , \qquad (8)$$

where $x_1 = n_1/(n_1+n_2)$, *etc*. Then the change of entropy of mixing will be

$$dS = -\frac{\partial}{\partial T}(dF) = -R(x_1 \ln x_1 + x_2 \ln x_2) - \\ -\frac{\partial}{\partial T}(\lambda x_1 x_2) \quad . \tag{9}$$

When $\lambda > 0$, *i.e.*, the interaction is an attractive force, probably, $dS < 0$. For instance, for $x_1 = x_2 = ½$,

$$dS = R\ln 2 - \frac{1}{4}\frac{\partial\lambda}{\partial T} \tag{10}$$

When $\lambda > (4R\ln 2)T$, $dS < 0$ is possible. This example is also representative for substitutional alloys, using ferromagnets, *etc*. (Fast 1962).

For a non-ideal gas, the thermodynamic potential (Reichl 1980) is

$$\Omega = -PV = -\langle N\rangle kT \sum_{l=1}^{\infty} B_l(T)\left(\frac{\langle N\rangle}{V}\right)^{l-1}, \tag{11}$$

where $B_l$ is the so called virial coefficient . Assuming $\langle N\rangle/V$ = constant, the entropy is

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_x = \frac{\partial}{\partial T}\left\{\frac{kT}{V}\sum_{l=1}^{\infty}\left[C^l B_l(T)\right]\right\} \\ = \frac{k}{V}\sum_{l=1}^{\infty} C^l \left(B_l + T\frac{\partial B_l}{\partial T}\right) \tag{12}$$

Let

$$V = 4\varepsilon\left[\left(\frac{\sigma}{Q}\right)^{12} - \left(\frac{\sigma}{Q}\right)^{6}\right] \tag{13}$$

be the Lennard-Jones 6-12 potential (Reichl 1980), then

$$B_2 = b_o \sum_{n=0}^{\infty} \alpha_n \left(T^*\right)^{-\frac{2n+1}{4}},\ B_3 = b_o^2 \sum_{n=0}^{\infty} \beta_n \left(T^*\right)^{-\frac{n+1}{2}} \\ \left(T^* = \frac{kT}{\varepsilon}\right) \quad , \tag{14}$$

$$S = \left(\frac{kC}{V}\right)\left[\begin{array}{l} 1 + Cb_o \sum_{n=0}^{\infty} \alpha_n \frac{3-2n}{4}\left(T^*\right)^{-\frac{2n+1}{4}} + \\ + C^2 b_o^2 \sum_{n=0}^{\infty} \beta_n \frac{n+3}{2}\left(T^*\right) \end{array}\right]^{\frac{n+1}{2}} \tag{15}$$

If $B_l$ for $l \geq 3$ is neglected,

$$S = \frac{kC}{V}\left\{1 + Cb_o\left[\begin{array}{l} \alpha_o \frac{3}{4}\left(T^*\right)^{-1/4} + \frac{1}{4}\alpha_1\left(T^*\right)^{-3/4} - \\ -\frac{1}{4}\alpha_2\left(T^*\right)^{-5/4} - \frac{3}{4}\alpha_3\left(T^*\right)^{-7/4} - \ldots \end{array}\right]\right\}. \tag{16}$$

Since $\alpha_n > 0$ for $n = 0$, and $\alpha_o < 0$ for $n > 0$, and $b_o = 2\pi\sigma^3/3 > 0$, all terms of the entropy (16) are positive except the $\alpha_1$ term. Therefore, the entropy is positive, and decreases as the temperature rises and $T^{-u}$ decreases. This is consistent with the formula $dS = dQ/T$ .

A galaxy may be regarded as an isolated system (Harwit 1973). Based on the virial theorem, the total energy of the system is finite. For an inverse square law force, as in gravitation or electrostatics, the average potential energy is $V = -2K$ (Harwit 1973). When the stars are formed from gases, and the galaxies are formed from a medium in the universe, an assembly of molecules is considered, their average kinetic energy $K$ per mole is

$$K = 3\left(c_p - c_\nu\right)\frac{T}{2} = 3(\gamma - 1)\frac{c_\nu T}{2}\ . \tag{17}$$

$$V = -3(\gamma - 1)U\ , \tag{18}$$

where $\gamma = c_\nu T$ is the internal energy. The total energy per mole is

$$E = U + V = -(3\gamma - 4)U = \frac{(3\gamma - 4)V}{3\gamma - 3}\ . \tag{19}$$

For C> 4/3, E is always negative, and the system is bound. If the system contracts and the potential energy changes by $\Delta V$ , then

$$\Delta E = \frac{(3\gamma - 4)\Delta V}{3\gamma - 3} = -(3\gamma - 4)\Delta U\ . \tag{20}$$

Hence, the internal energy increases by

$$\Delta U = -\frac{\Delta V}{3\gamma - 3}, \tag{21}$$

due to a rise in temperature. As the protostar contracts to form a star, it therefore becomes hotter and hotter. We may describe the formation of stars through the compression of cool gas clouds, since, as it collapses, the protostellar cloud becomes hotter and hotter (Harwit 1973). Thus, the disordered protostellar cloud forms regular stars through self-interactions in the evolutionary process.

According to the second law of thermodynamics, the universe must proceed irreversibly from a state of order and low entropy toward a state of disorder and high entropy. Eventually, when the universe has reached a state of maximum entropy, it should be a uniform gas with a uniform constant temperature. But, low entropy stars form from high entropy gas clouds. Wesley (1989, 1991) has stated the primary law for ordering processes in nature: statistical thermodynamic systems open to deep space with temperatures greater than 2.7 K proceed toward states of lower entropy. All observable portions of the universe thus proceed toward states of greater thermodynamic order, lower entropy, or less chaos. Wesley (1996) considered that although the net entropy change per unit mass is negative when a gas condenses into a star, the entropy production that is radiated off is two orders of magnitude greater than the entropy reduction, so the second law of thermodynamics is not violated. Moreover, Wesley discussed the relevance of fluctuations away from equilibrium for cosmology, and the generalization of entropy to non-equilibrium situations.

Further, the potential (13) agrees well with a very strong repulsive hard-core and a short-range attractive force, which just corresponds to the microscopic strong interaction. Weinberg has proposed a generalized theory of nonrelativistic nonlinear quantum mechanics as a framework for the development and analysis of experimental tests of the linearity of quantum mechanics (Weinberg 1989). However, Peres (1989) has proven that nonlinear variants of the Schroedinger equation violate the second law of thermodynamics. We are sure that a nonlinear development of various theories is a necessary direction. The above contradiction shows that the second law of thermod namics seems to exclude *i.e.* interactions).

the computer experiments show that the coupling together

the degree of order in the composite system (Shaw 1987).

symmetrical state in simple systems.

exist in an isolated system, if a mechanism produces a *e.g* g netic body, .) that increases entropy, a reverse mech - *e.g* temperature, paramagnetic body, ) to decrease the e - m

$$S = -\frac{¶V}{¶T} \qquad (22)$$

$S_2 > S_1$ when $¶V_2/¶T_2 < ¶V_1/¶T_1$ ; conversely, $S_2 < S_1$ when $¶V_2/¶T_2 > ¶V_1/¶T_1$ .

In a system composed of two subsystems which are not independent, the subadditivity states that

$$S(r) \leq S(r_1) + S(r_2), \qquad (23)$$

where $r = lr_1 + lr_2$ (Wehrl 1978). This shows that the entropy decreases with the internal interaction. Not only is this conclusion the same with the conditioned entropy on $r_1$ and $r_2$, but it is also consistent with systems theory in which the total may not equal the sum of parts.

## 3. Discussion and conclusion

Of course, the above examples are not already under the thermodynamic equilibrium condition. For non-equilibrium states statistic mechanics defines entropy as $S = k \log W$ (Pauli 1973). In the evolutionary process and phase transition, the systems cannot be in thermal equilibrium; this is true for various systems in biology and society. In fact the self-control mechanism in an isolated system may produce a degree of order. If it does not need the input energy, at least in a given time interval, self-control will act like a type of Maxwell demon, which is just a type of internal interaction. The demon may be a permeable membrane. For the isolated system, it is possible that the catalyst and an other substance are mixed to produce new-order substance with smaller entropy. Ordering is the formation of structure through self-organization from a disordered state.

The second law of thermodynamics is a probability law. The transition probability from molecular chaotic motion to regular motion of a macroscopic body is very small. But, this result may not hold if interactions take place within a system. According to the Boltzmann and Einstein fluctuation theories, all possible microscopic states of a system are equal-probable, and the entropy in the equilibrium state possesses a maximum value, while it is known from statistical mechanics that fluctuations of entropy may occur (Haken 1977). Schulman (1991) discussed the thermodynamic arrow of time, and the existence and abundance of special states which are constrained with much greater probability. In a system with internal interactions, the fluctuation can be magnified, and when phase transition occurs, self-organization will take place, as in synergetics. Simultaneously, the entropy will decrease continuously, and a final ordered state, with a lower entropy, will be reached. In this case various microscopic states are not equally probable. If entropy is seen as a degree of freedom, the interaction will reduce the degrees of freedom.

In short, thermodynamics and its second law are based on certain prerequisites, such as statistical independence, *etc*. We think that the applicability of the entropy increase principle should be tested again (Chang 1994). If there are interactions among the subsystems in an isolated system: 1. some generalized second law of thermodynamics may not be applicable; 2. the entropy increase principle in a non-equilibrium process may not hold. The possible mechanism behind conclusions is fluctuation and self-interaction, from which self-organization may form a lower entropy state.

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