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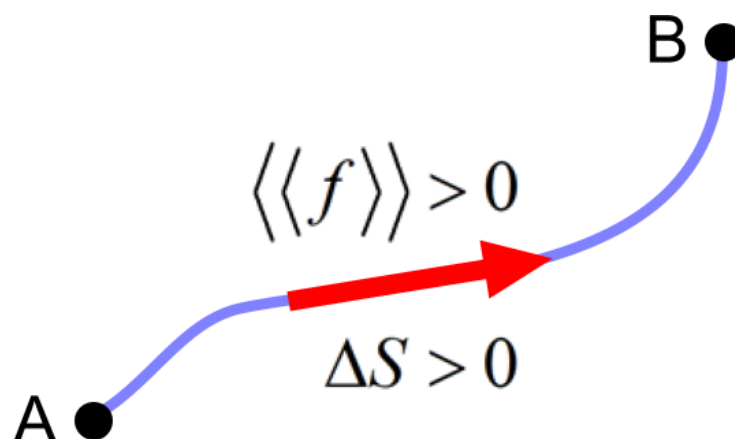# The second law of thermodynamics as a force law

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Abstract: The second law of thermodynamics states the increase of entropy, $\Delta S > 0$, for real processes from state A to state B at constant energy from chemistry over biological life and engines to cosmic events. The connection of entropy to information, phase-space and heat is helpful, but does not immediately convince observers of the validity and basis of the second law. This gave grounds for finding a rigorous, but more easily acceptable reformulation. Here we show using statistical mechanics that this principle is equivalent to a force law $\langle\langle f \rangle\rangle > 0$ in systems where mass centres and forces can be identified. The sign of this net force - the average mean force along a path from A to B - determines the direction of the process. The force law applies to a wide range of processes from machines to chemical reactions. The explanation of irreversibility by a driving force appears more plausible than the traditional formulation as it emphasizes the cause instead of the effect of motions.

Abstract Graphic

Keywords: statistical mechanics; irreversibility; arrow of time; chemical dynamics

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1. Introduction

The second law of thermodynamics (SLT) is a fundamental and general empirical law of physics that is being discussed since it was articulated by Clausius [1] long time ago. It states the permanent growth of entropy in the dynamics of all macroscopic systems from chemistry over biological life and engines to cosmic events and thus claims the existence of an arrow of time which seems to contradict the time-reversibility of classical and quantum mechanical theory. A second difficulty lies in the abstractness of the entropy concept. The connection with information and phase-space volume is still too far apart from typical real processes. The increase of that volume after release of a constraint can be considered as self-evident [2]. Mathematically it was in fact shown that the onset of motion after release of a constraint follows the SLT [3], but this glance at a particular situation does hardly increase the plausibility for the fact that the increase of entropy represents the dynamical background of the everyday macroscopic world.

The SLT represents a universal dynamic law of macroscopic systems without explicitly referring to any force. Entropic forces, however, are known to be responsible for the isothermal pressure of an ideal gas, elasticity of rubber [4] and macromolecular structure via internal fluctuations [5]. In these examples, entropy essentially provides static forces stabilizing equilibria. This also holds for entropic hydrophobic force in aqueous solutions which, however, is also qualitatively considered as a cause of the protein folding process [6].

It was the aim of this study to find a clear, general and didactically accessible relationship between the change of entropy and a driving force that can be made responsible for the process. Such a relationship is not a theoretical proof of the second law, but it leads to an alternative formulation as a force law. The new look at the second law is also elucidating the occurrence of irreversibility.

The concept of a force is, of course, restricted to classical mechanics. Therefore the following considerations apply from macroscopic processes down to molecular motions and reactions as long as they occur in the electronic ground state where, according to the Born-Oppenheimer approximation, nuclei effectively move on a potential energy surface. It is also assumed that classical statistical mechanics applies, which will be discussed later in the context of chemical reactions. The generalization to real quantum phenomena seems possible, but is beyond the scope of this work.

2. General approach

Let us consider a small system S characterized by a only a few coordinates $\mathbf{x} = (x_1 ... x_M)$ like the position of pistons or similar moving parts, but also of interatomic distances involved in a chemical reaction. The composite system consists of a large number of $N \gg M$ particles where the environment has spatial and momentum coordinates $\mathbf{q} = (q_1 ... q_{3N-M}), \mathbf{p} = (p_1 ... p_{3N-M})$ that are to be treated statistically. It is assumed that there is a Hamiltonian function

$$H(\mathbf{q},\mathbf{p};\mathbf{x}) = K(\mathbf{q},\mathbf{p}) + v(\mathbf{q},\mathbf{p},\mathbf{x}) \qquad (1)$$

with $\mathbf{x} = (x_1 ... x_M)$ as parameters and a classical treatment is suited to treat equilibria and processes. $K(\mathbf{q},\mathbf{p})$ is the kinetic and $v(\mathbf{q},\mathbf{p},\mathbf{x})$ the potential energy. Sometimes the Hamiltonian can be written $H(\mathbf{q},\mathbf{p};\mathbf{x}) = H_s(\mathbf{x}) + v_{se}(\mathbf{q},\mathbf{p},\mathbf{x}) + H_e(\mathbf{q},\mathbf{p})$ where H_e is the Hamiltonian of the environment, v_{se} the

interaction with the system S and H_e the internal energy of the system. At macroscopic systems, for instance, H_s describes gravity and internal interactions of moving parts. At chemical reactions the decomposition is not useful as we will consider composite systems with global energy or temperature, and no separate energy can be attributed to the parameters of the small system S.

For the time being, we define states like A, B by representative configurations $\mathbf{x}$, while a process is defined as a transition $A \rightarrow B$, for instance. Fig. 1 illustrates the existence of a few states near the starting state A and pathways connecting them.
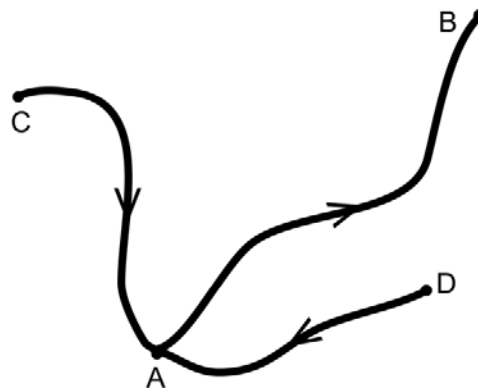

Figure 1. Pathways including state A. For possible processes, the arrows show the preferential direction which can be derived from the second law of thermodynamics or the new force law.

The Hamiltonian $H(\mathbf{q},\mathbf{p};\mathbf{x})$ yields forces $\mathbf{F}(\mathbf{q},\mathbf{p};\mathbf{x}) = -\nabla_x H(\mathbf{q},\mathbf{p};\mathbf{x})$. The average behaviour is determined by the potential of mean force (PMF) $\Pi(\mathbf{x})$ via the mean force itself, $\langle \mathbf{F}(\mathbf{x}) \rangle_{\in} = -\nabla_x \Pi(\mathbf{x})$, which arises from integration over $(\mathbf{q},\mathbf{p})$ in the statistical ensemble $\in$, examples will be given below. It vanishes at a stable thermodynamic state which may be due to a constraint or occurs spontaneously and enables definition of thermodynamic potentials.

We now consider a process where the system follows a path from A to B which is defined by $\mathbf{x}(l), 0 \leq l \leq L$, $\mathbf{x}_A = \mathbf{x}(0)$ and $\mathbf{x}_B = \mathbf{x}(L)$ being representative positions. The definition allows simultaneous and/or subsequent motions of mass centres. The direction is given by increasing l, and L is the length of the path as $|d\mathbf{x}/dl| = 1$. The component of the force in the direction of the path is $f(l) = \mathbf{F}(\mathbf{q},\mathbf{p};\mathbf{x}) \cdot d\mathbf{x}/dl$. The average along the path of the corresponding mean force $\langle f(l) \rangle_{\in}$ becomes

$$\left\langle \langle f \rangle_{\in} \right\rangle_{AB} = L^{-1} \int_0^L \langle \mathbf{F}(\mathbf{x}) \rangle_{\in} \cdot \frac{d\mathbf{x}}{dl} dl = -L^{-1} \left(\Pi(\mathbf{x}_B) - \Pi(\mathbf{x}_A) \right) \equiv -\Delta\Pi_{AB}/L. \tag{2}$$

Note that the dot product here denotes the M-dimensional inner product. Interestingly, the average mean force is independent of the pathway itself and depends only on the difference of the PMF at the end points and the direction of the process, $\left\langle \langle f \rangle_{\in} \right\rangle_{BA} = -\left\langle \langle f \rangle_{\in} \right\rangle_{AB}$. The crucial result is the equivalency

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$$\left\langle \left\langle f \right\rangle_{\in} \right\rangle_{AB} > 0 \;\Leftrightarrow\; \Delta\Pi_{AB} < 0 . \tag{3}$$

This is the very general form of the force law which, for the sake of clarity, will be illustrated by considering two important ensembles.

3.   Results

3.1 Microcanonical ensemble: the force law and the increase of entropy

For an (NVE) ensemble entropy can be written

$$S(\mathbf{x}) = k_B \ln \int_V d\Gamma \, \Theta\left(E - H\left(\mathbf{q},\mathbf{p};\mathbf{x}\right)\right). \tag{4}$$

The differential phase volume is $dΓ = dq^{3N-M} dp^{3N-M} / h^{3N-M}$ for non-identical particles and has to be adapted for other cases, h the Planck constant and k_B the Boltzmann constant. At chemical reactions, it is possible to deal with constant particle numbers n_i and $N = \sum n_i$ when not molecules, but nuclei are treated as different kinds of particles.

Θ is the Heaviside jump function the derivative of which is the functional δ. When entropy is differentiated with respect to $\mathbf{x}$, one obtains $\nabla_x S(\mathbf{x}) = \left\langle \mathbf{F}(\mathbf{x}) \right\rangle_{NVE} / T(\mathbf{x})$. The positive quantity $T = (dS/dE)^{-1}$ is the temperature of the complete system and can, therefore, be considered as constant in the thermodynamic limit of large environments. The PMF delivering the mean force is $\Pi(\mathbf{x}) = -TS(\mathbf{x})$ and finally yields according to eq. (3) the crucial statement

$$\left\langle \left\langle f \right\rangle_{NVE} \right\rangle_{AB} > 0 \;\Leftrightarrow\; \Delta S_{AB} > 0 . \tag{5}$$

Notoriously the claim of the SLT for a real process is an increase of entropy, $\Delta_{AB} S > 0$. This is apparently equivalent to the force law for a real process, $\left\langle \left\langle f \right\rangle_{NVE} \right\rangle_{AB} > 0$, which claims a positive net force, i.e. average mean force along any pathway $A \rightarrow B$.

It is easily seen that the force law eq. (5) holds even at processes in small environments where temperature does not remain constant, when the average eq. (2) along the path is taken with weights proportional to $1/T(\mathbf{x})$.

3.2 Isobaric-isothermal ensemble: the force law and the decrease of Gibbs energy

In life science and chemistry the (NPT) ensemble applies to the majority of cases where temperature T and pressure P are maintained by the environment. Here the PMF is known to be the Gibbs energy[7] defined as

$$G(\mathbf{x}) = k_B T \ln \int d\Gamma \int dV \exp{-\beta\left(H\left(\mathbf{q},\mathbf{p};\mathbf{x}\right) + PV\right)}. \tag{6}$$

In fact differentiating eq. (6) shows that the ensemble mean of the force is $\langle \mathbf{F}(\mathbf{x}) \rangle_{NPT} = -\nabla_x G(\mathbf{x})$ and therefore the PMF equals the Gibbs energy $\Pi(\mathbf{x}) = G(\mathbf{x})$. Then it follows from (3) that a real process is characterized by two equivalent assertions

$$\left\langle \left\langle f \right\rangle_{NPT} \right\rangle_{AB} > 0 \iff \Delta_{AB} G < 0 \ . \tag{7}$$

Here the force law is equivalent the well-known claim for Gibbs energy that it will decrease at a real process, which is a consequence of the SLT for the (NVE) ensemble.

Interestingly, the mean force can be measured either experimentally in the case of macroscopic systems like engines, or computationally for microscopic systems like protein nanomachines or even atoms at a chemical reaction. The principle is like this: the system is stopped at some position $\mathbf{x}$ and the force required for that purpose, the so-called mean constraint force $\mathbf{F}_c$, is measured which coincides with the negative mean force as [7-9]

$$\left\langle \mathbf{F}(\mathbf{x}) \right\rangle_\in = -\left\langle \mathbf{F}_c(\mathbf{x}) \right\rangle_\in \tag{8}$$

at Cartesian or distance coordinates [10]. The constraint force usually exhibits strong fluctuations and a convergence towards the mean that depends on relaxation processes of the environment.

3.3 Irreversibility

It was shown above that the integral over the mean force along any path from A to B yields the same increase or decrease $\Delta\Pi_{AB}$ in the PMF, but the course of $\Pi(\mathbf{x}(l))$ and the length of the path can be very different. This is illustrated in Fig. 2 for two different pathways.
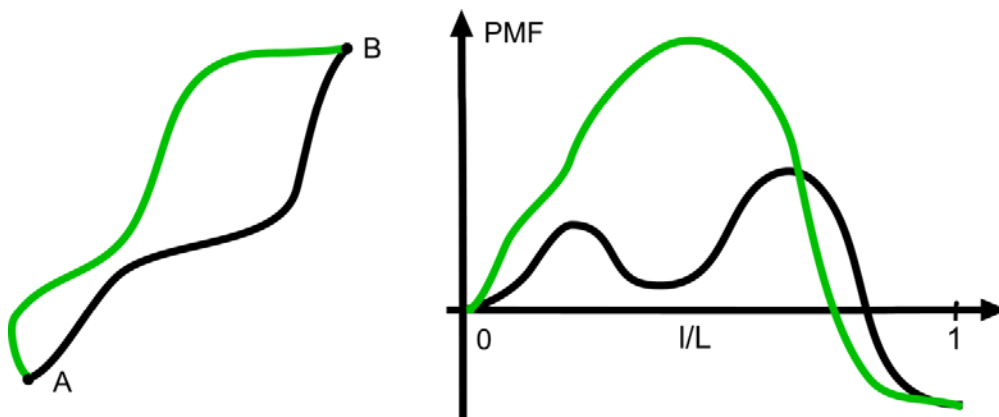

Figure 2. Alternative pathways from A to B (left) with respective profiles of the potential of mean force. In either case the identical decrease of the PMF implies that the average mean force - i.e. the negative derivative - along the path is positive and drives the motion from A to B. Likewise the positive average mean force implies the decrease of the PMF.

According to theories of activated processes like chemical reactions, the rate for a transition is determined by the profile of the PMF, for instance $-TS(\mathbf{x})/k_B$ or $\Delta G(\mathbf{x})$, and the starting conditions. The maximum rate k depends on the height of the maximum barrier, and therefore certain pathways will be taken more often than others due to bottleneck barriers that are hardly overcome. Comparing the rates for process $A \rightarrow B$ and the reverse process $B \rightarrow A$ between equilibrium states one has, for instance in the isobaric-isothermal case, the familiar relation

$$\frac{k_{BA}}{k_{AB}} = \exp\left(\Delta G_{AB} / k_B T\right). \tag{10}$$

Since for a real spontaneous process $\Delta G_{AB} < 0$, there is in general a time-asymmetry with a lower rate k_{BA} for the reverse process. Many chemical reactions are called irreversible in the sense that back-reactions plays practically no role, but there are also reactions with considerable back-reaction rates that result in observable equilibria $A \leftrightarrow B$. Factual irreversibility arises at macroscopic transitions. If for instance, a realistic ΔG_{AB} of -1 Joule is measured and a rate of one per hour at 300 K, then the back-reaction is in actual fact impossible since $k_{BA} = \exp\left(-2 \times 10^{20}\right) h^{-1}$. Thus macroscopic processes with typical change in entropy or Gibbs energy are irreversible. The force law eq. (7) indicates that the cause is an unfavourable net force that opposes the back-reaction.

4. Discussion

We have addressed the SLT using the concept of pathways and their characterization by mean forces depending on the ensemble chosen. As a result we propose a new force law stating that a real thermodynamic process is based on a net force with the right sign. This alternative and equivalent formulation of the SLT holds for processes from machines down to chemical reactions as long as they can be parametrized by motions of a few mass centres of a much larger system. Heat conduction itself and photochemical reactions are not included as forces do not enable a reasonable formulation of such processes.

The application to chemical reactions including processes of biological life like enzyme catalysis, where bonds are broken and others are formed, deserves particular consideration. For a given Born-Oppenheimer potential energy function (BOP) quantum mechanics still requires consideration of tunnelling and transmission coefficients when calculating transition rates [11], zero-point energies and entropies when calculating equilibrium quantities as we do here. Without quantum mechanical correction, BOP would yield negative entropy [12] and too low energy for chemical bonds and is only an approximation to the classical force field $v(\mathbf{q}, \mathbf{p}, \mathbf{x})$ that produces correct Gibbs bond energies. This force field will differ from BOP by shallower potential wells for chemical bonds (and bond angles) and slightly depend on temperature. Considerable efforts are still made to construct such force fields [13]. For the force law discussed here it only matters that quantum mechanics suggests the existence of a classical force field that yields the correct PMF in eq. (2).

Newton's second law connects force with acceleration by a rigorous analytic relation independent of the direction of the motion. It is time-reversible since it holds for either direction and does not imply that

motion follows the force. The new force law $\langle\langle f \rangle\rangle > 0$, however, which is equivalent to the SLT $\Delta S > 0$ in the world of mass centres, is a statistical statement that reflects the behaviour for the underlying ensemble. Given two states A and B, it gives preference to a particular direction, the other direction being drastically suppressed in macroscopic circumstances. On the average, motion follows the mean force. Apparently the arrow of time is represented by the arrow of the net force originating from a realistic ensemble. The deeper reason for irreversibility is, of course, the occurrence of relaxation which is always tacitly assumed when using ensembles and mean values.

The counterexample of a time-reversible system connected with an unrealistic probability distribution is the completely undamped pendulum. There it is easily seen taking the time average that the system is preferably found at high potential energy. Only if damping is introduced by coupling to a heat bath, reversibility is lifted and a realistic distribution emerges.

Despite the mathematical equivalency, there is a clear difference between the traditional form of the SLT and the force law. While the SLT talks about entropy as the characteristic product of a real process, the force law emphasizes the cause of real processes by stating that a net driving force is needed and determines the direction. It offers the didactical advantage of clarifying much of the SLT on the familiar basis of forces before introducing entropy as a concept of statistics or information theory. One may hope that the SLT as a force law is a more plausible and more easily acceptable explanation of reality.

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