"Ueber die mechanischen Analogien des zweiten Hauptsatzes der Thermodynamik," J. f. d. reine u. angew. Math. **100** (1887), 201-212.

On the mechanical analogies for the second law of thermodynamics

(By *Ludwig Boltzmann* in Graz.)

Translated by D. H. Delphenich

Among all pure mechanical systems for which equations exist that yield analogues for the so-called second law of the mechanical theory of heat, it seems to me that the one that I (*) and *Maxwell* (**) have examined in several treatises plays the most important role, by far. Not only is the analogy with the equations of the theory of heat true for all such systems without exception, and for all equations that determine their behavior without exception, but it is also true for most of the other systems, to the extent that under mechanically simple conditions they will exhibit far-reaching and undeniable analogies that are subordinate to what *Maxwell* and I considered as special cases. Moreover, other mechanical grounds exist that make it likely that warm bodies generally carry with them the character of the latter systems.

In the last-cited treatise, I merely cited the general theorem that relates to the convertibility of internal energy into external work performed for these systems without proof. We first imagine an arbitrary mechanical system whose internal forces are conservative. The relative positions of all the parts of the system shall be determined by b coordinates $p_1, p_2, p_3, \ldots, p_b$, whose differential quotients with respect to time, which we would also like to call the *velocities*, shall be called $p_1', p_2', \ldots, p_b'$. Let the internal and external forces that act upon the system be given as functions of the coordinates, and in addition, let the total entire energy content of the system be given. That will correspond to a warm body for which the internal nature, external forces, and temperature are given. Experience teaches us that the behavior of the warm body is determined completely, as opposed to that of the mechanical system, which can be completely different according to its initial state. However, a wide variety can exist in the number of initial conditions that are required in order to determine the form of the motion of the

(*) "Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiallen Punkten," Wien Sitzber., Bd. LVIII, Jahrg., 1868.

"Einige allgemeine Sätze über Wärmegleichgewicht," Wien Sitzber., Bd. LXIII, Jahrg., 1871.

"Analytischer Beweiss des zweiten Hauptsatzes der mechanischen Wärmetheorie aus den Sätzen über das Gleichgewicht der lebendigen Kraft," *Ibidem.*

"Ueber die Eigenschafter monocyklischer und anderer damit verwandter Systeme," Wien Sitzber., Bd. CX, Jahrg., 1884; this Journal, Bd. 98.

(**) "On *Boltzmann's* Theorem on the average distribution of energy in a system of material points." [Cambridge Philosophical Transactions, vol. XII, part. III), *Wiedemanns* Beiblätter, Bd. **5** (1881), 403.]

mechanical system. The motion of the system is determined by $2b$ first-order differential equations in the $2b$ independent variables $p_1, p_2, \ldots, p_b, p'_1, p'_2, \ldots, p'_b$, and the independent variable time t. Their integrals will include $2b$ integration constants, to which, one can always add a constant to t, since we exclude the case in which the equations of motions include the absolute value of time explicitly; we would like to denote it by $-\tau$. From the usual rules, $2b$ initial values must be given in order to determine the integration constants, and thus the values of all coordinates and velocities for $t = 0$. Now, since one of these initial values determines the value t, and this gives merely when the motion takes place, the form of the equations (i.e., the form and position of the paths in space and the type and manner by which they are described) are determined by $2b - 1$ values, or speaking more generally, along with the differential equations for the motion, $2b - 1$ mutually independent quantities must be given for the purpose of the complete determination of the form of the motion, and we would like to call these quantities *parameters*. However, the quantity t merely determines the time when the path is defined. Nonetheless, exceptions can and will occur, in general. Namely, one can find integral equations that can be satisfied by not just one, or a finite number of combinations of coordinates and velocities, but by an infinite number of them, such as the way that the equation $\arcsin x = A \arcsin y$ will be satisfied by an infinite number of value pairs for x and y when A is irrational. If we think of all the integration constants as being given then we can express any of the variables $p_1, p_2, \ldots, p_b$ (e.g., p_1) as a function of the second one (e.g., p_2) and the $2b-1$ integration constants when we eliminate $p_3, p_4, \ldots, p_b$ and $t - \tau$. Now, the resulting equation can be arranged such that it will be fulfilled by a single number or a finite number of values of p_1 for given values of the integration constants. However, like the equation $\arcsin x = A \arcsin y$ that was cited above, it can also be satisfied by a sequence of values of p_1 that go to each other continuously, such that p_1 is merely included between certain limits, inside of which it is capable of assuming an arbitrary value.

An example of this is given by the motion of a material point in a plane with rectangular coordinate x, y, upon which the forces $C = -a^2 x$, $Y = -b^2 y$ act in the two coordinate directions, which then moves according to the same laws as the point of light in the *Lissajous* figures. When a and b, and thus, the period of oscillation of the two tuning forks, are commensurable, the material point will describe a closed curve. If we then choose the two rectangular coordinates x and y for p_1 and p_2 then, as long as the values of the integration constants and x are given, that of y will be restricted to a finite number of values. By contrast, if a and b are incommensurable then the material point will traverse the entire interior of a surface that lies in a rectangle over a very long time interval, and as soon as x is given, y is merely included between two limits.

In that case, we would like to say that one of the integral equations is *infinitely multi-valued*. Precisely analogous cases also appear for central motion: If the path is a closed one then none of the integrals of the equations of motion will be infinitely multi-valued, while the latter case will come about as long as the path is not closed. Whenever an integral is infinitely multi-valued, the number of independent variable parameters that are required for the determination of the form of the motion will be one less, and thus, only

$2b - 2$ (*). In the first-cited example, the three integration constants are two energies of motion in the directions of the *X* and *Y* axes and the phase difference between these two motions. If the path is closed then a knowledge of the three values of these quantities, which play the roles of three completely-determined variables, is necessary for the determination of the form of the motion.

However, if *a* and *b* are incommensurable, so the path is not closed, then the knowledge of the values of the first two integration constants will suffice to determine the motion completely. The first two integration constants are thus what I called the parameters of the path; no matter what the initial phase difference of the motions in the two coordinate directions might be, in the course of an infinitely-long time interval, all possible phase differences will always occur. All paths for which the values of the first two integration constants are the same will go to each other after a finite or infinite time interval, so all of the remaining quantities will then determine only the time interval over which the path is traversed. We can also say: When the path is closed, all pairs of values of *x* and *y* that correspond to a path will define a manifold of only one dimension. If the two energies in the two coordinate directions are given then infinitely many paths with different forms will be possible. By contrast, in the second case, all values of *x* and *y* will be traversed that are actually compatible with the two equations of the *vis viva*. The third integral of the equation of motion will lose its meaning. The moving pair of values of *x* and *y* thus now defines a manifold of two dimensions. Central motion with closed or unclosed paths will also behave similarly.

A second integral of the equations of motion can be infinitely multi-valued in just the same way. For central motion, there can be a cylinder with an infinitely-small base of arbitrary form, moreover (e.g., perpendicular to the plane of the path), on whose circumference, the moving point will be reflected like an elastic ball. In that way, after a very long motion, the values of the surface velocity would be changed again and again, and in the course of a very long time, they would assume an infinite sequence of values that went into each other continuously, such that the surface equation would also lose its meaning. (Cf., my treatise: "Lösung eines mechanischen Problems," Wiener Sitzungsberichte, Bd. 58, II Abtheilung, Jahrgang 1868.) By the same device, a single equation for the *vis viva* would enter in place of the two equations. Moreover, if that cylinder had a position such that it would be met by all paths that are compatible with the equation of the *vis viva* (so for central motion, it would lie infinitely close to the circular path and for the *Lissajous* motion, it would lie infinitely close to the coordinate origin) then in the course of time, in fact, all possible combinations of values of x, y, dx / dt and dy / dt that are compatible with the equation of *vis viva* would be traversed.

We would now like to consider the most general case, for which we assume that *k* integrals of the equation of motion are infinitely multi-valued. After eliminating $t - \tau$, only $2b - k - 1$ integral equations would then remain, which would not be infinitely multi-valued, and the variables could run through all possible values that are compatible with the $2b - k - 1$ equations in the course of time. In that way, we can imagine a system in which $k = 2b - 2$, so it will be one in which all possible values of the variables will be

(*) In general, it can happen that when the equations of motion and the $2b - 2$ parameters are given, the form of the motion is not determined uniquely, but a finite number of forms of motion are possible, such that in order to obtain a unique determination, the limits between which the last integration constants lie must be given.

traversed that are compatible with the equation of the *vis viva*. An example of this is given by either the *Lissajous* motion that was perturbed by an infinitely thin cylinder that was just discussed or central motion. All motions for which $b = 1$ serves as a much simpler example. Such a system would take on the same properties that warm bodies exhibit in experiments, to the extent that its state would be determined completely when one knew the total energy that was contained within it, in addition to the external and internal forces. The probability of the different states, as well as the total behavior of such a system, can now be calculated with particular ease. (Cf., my cited "Studien," section III and my treatise "Einige allgemeine Sätze über Wärmegleichgewicht," section II.) However, warm bodies even possess a property of much greater generality, in that the different phases that its state of motion assumes in the course of time are not experimentally noticeable, but due to the large number of atoms in it, as soon as any atom enters into another phase state, in exchange, it will again assume a neighboring phase state that the former previously possessed. It undoubtedly follows from this that only completely random differences in the state of warm bodies will be brought about by the different initial conditions, while all essential and observable properties of them will depend upon merely the total value of its energy, in addition to the internal and external forces. The precise mathematical expression of just this situation encounters complications, however, and can best be formulated by means of the following artifice. (Cf., on this, my previously-cited treatise "Einige allgem. Sätze über Wärmegleichgewicht," section I; *Maxwell's* cited treatise, page 549.)

In place of a single system, we choose infinitely many systems that are completely the same, and in each of which the same energy is contained, as well, but which possess all possible initial states, moreover. All of them should experience the same energy increase, and the external conditions should change in the same way for all of them. All properties that are independent of the random initial conditions must now also belong to the totality of systems in the same way. For example, if the work that a system exerts against any external force were to contain the mean energy that a component of the system contains, or similarly, depend upon the initial state of the system essentially, then the mean value of these quantities for the totality of systems would naturally not equal the value of it for a single system. However, if the values of these quantities do not depend upon the initial state in a perceptible way then that mean value would have to be equation to the value of the same quantity for each individual system. It is thus not at all necessary for us to calculate the values of these quantities for every individually-determined system that is subject to initial conditions, but it will suffice to calculate its mean value for the entire totality of systems. This calculation will be made easier by the fact that it is left entirely to our discretion how we would like to define the totality – i.e., if N is the number of systems, and dN is the number of systems for which the initial state lies between certain infinitely-close limits then dN can contain an entirely arbitrary function of the variable that determine the initial state. For a suitable choice of that function, we can now make it possible for equations to be true for the totality of all systems that have the same simplicity as for a system that runs through all possible states that are compatible with the equation of *vis viva* by itself. Now, since we have proved that for each individual system, the value of the quantities that are independent of the initial conditions is equal to the mean value of the same quantities for an arbitrarily defined totality of systems, it will suffice to determine the mean value of such quantities for that totality for which the calculation becomes as simple as possible. We would now like to make such a choice.

We thus imagine that we are given, not a single such system, but infinitely many (N) equally-arranged systems. Moreover, we follow precisely the method that was given by *Helmholtz* (*), by which, at a single stroke, we will bring a hitherto-unsuspected clarity to all of these investigations. We divide the coordinates of each system into two classes: a of them $s_1, s_2, \ldots, s_a$ shall be completely constant, as long as the state of the system is unvarying, and change into another state under a transition only extremely slowly. These coordinates shall also have precisely the same values for all N systems, and their values for all N systems shall change in precisely the same way. In the theory of heat, they characterize what one cares to refer to as the external conditions under which the warm body is found. By contrast, the motion of heat shall be represented by rapid variations of the second class of coordinates $p_1, p_2, \ldots, p_b$. The differential equations that determine the variation of these coordinates shall likewise be precisely the same for all N systems. All forces that strive to change the value of the rapidly-varying quantities shall be called internal forces of the system. By contrast, the ones that act upon only the slowly-varying coordinates shall be called external forces. The initial values of the rapidly-varying coordinates shall be as diverse as possible for the different systems; now, a totality that is especially convenient is characterized by the fact that the number of those systems for which the initial values of the coordinates lie between the limits:

$$(1) \qquad p_1 \text{ and } p_1 + dp_1, \qquad p_2 \text{ and } p_2 + dp_2, \qquad \ldots, p_b \text{ and } p_b + dp_b,$$

and, at the same time, whose momenta lie between the limits:

$$(2) \qquad q_1 \text{ and } q_1 + dq_1, \qquad q_2 \text{ and } q_2 + dq_2, \qquad \ldots, q_{b-1} \text{ and } q_{b-1} + dq_{b-1},$$

is equal to:

$$(3) \qquad d\mathfrak{N} = N \cdot \frac{\dfrac{dp_1 \cdot dp_2 \cdot dp_3 \cdots dp_b \cdot dq_1 \cdot dq_2 \cdots dq_{b-1}}{p'_b}}{\iint \dfrac{dp_1 \cdot dp_2 \cdots dp_b \cdot dq_1 \cdot dq_2 \cdots dq_{b-1}}{p'_b}}.$$

The last momentum q_b is determined from the equation of *vis viva*. The integrations are all extended over all possible values of the variables that are run through during the motion of all systems. As *Maxwell* (*loc. cit.*, pp. 554, formula 28) has proved, if the distribution of systems is a completely stationary one – i.e., as long as the values of the slowly-varying coordinates are constant – the number of systems for which the coordinates and momenta lie between the limits (1) and (2) will always remain the same. (I have proposed the name of *ergode* for such a totality of systems.) In that regard, the totality of all N systems then possesses precisely the property of warm bodies that its properties remain unchanged under the invariability of the external conditions (viz., the s) and the conservation of energy. Therefore, if the value of any quantity does not change noticeably under unchanged external conditions and the conservation of energy, and also does not depend upon the initial conditions in a perceptible way then the value of these

(*) Sitzber. d. Akad. d. Wiss. zu Berlin, 6 March and 27 March 1884.

quantities for every individual system must equal its mean value for the totality of all N systems, which was already discussed thoroughly above. We can always transform the coordinates in such a way that the *vis viva* is represented as a sum of squares of momenta. With no loss of generality, we can then assume that for constant s the equation of energy for an individual system can be written in the form:

$$\frac{1}{2}(\mu_1 q_1^2 + \mu_2 q_2^2 + \cdots + \mu_b q_b^2) + V = L + V = E. \tag{4}$$

The force function V is a function of the slowly and rapidly varying coordinates. It can happen that some of the slowly-varying coordinates s do not appear in the coefficients μ; they then play the role of parameters that enter into the force function whose slow variation represents the slow change in the rule by which the external forces act. By contrast, other s can be true coordinates that will remain conserved for an unchanged state by suitable external forces (viz., the *Lagrange* forces) whose change, however, represents a change in spatial position for certain parts of the system. These s can also be included in the coefficients μ, along with the rapidly-varying coordinates. In order to avoid misunderstanding, I remark that I never make the *Helmholtz* assumption that V does not include the rapidly-varying coordinates, which is an assumption that is replaced with the consideration of a totality of very many systems by me. Since the number of systems for which the coordinates and momenta lie between the limits (1) and (2) remains stationary as long as E and s do not change, they are also always determined by the formula (1). The number of systems for which just the coordinates are included between the limits (1), while the momenta have arbitrary values is:

$$\left\{\begin{aligned} dN &= N \cdot \frac{dp_1 \cdot dp_2 \cdots dp_b \iint \cdots \dfrac{dq_1 \cdot dq_2 \cdots dq_{b-1}}{p_b'}}{\iint \cdots \dfrac{dp_1 \cdot dp_2 \cdots dp_b \cdot dq_1 \cdot dq_2 \cdots dq_{b-1}}{p_b'}} \\ &= N \cdot \frac{\dfrac{1}{\sqrt{\mu_1 \cdot \mu_2 \cdots \mu_b}} (E - V)^{\frac{b}{2}-1} dp_1 \cdot dp_2 \cdots dp_b.}{\iint \cdots \dfrac{1}{\sqrt{\mu_1 \cdot \mu_2 \cdots \mu_b}} (E - V)^{\frac{b}{2}-1} dp_1 \cdot dp_2 \cdots dp_b} \end{aligned}\right. \tag{5}$$

(Cf., *Maxwell, loc. cit.*, pp. 556, formula 41.)

We must now move on to the definition of one of the most important concepts, namely, the energy that is supplied from the outside under a transition from a certain state to another one that differs from it by infinitely little, and indeed, we say: $\delta_1 Q$ is the energy that is supplied by one of the $d\mathfrak{N}$ systems, $d\delta Q$ is the energy that is supplied by dN systems, and δQ is the energy that is supplied by all N systems. If all coordinates p and s have the same values in the varied state that they do in the original one then the energy that is supplied from the outside will obviously be equal to the increase in the *vis viva* δL; by contrast, if the values of the coordinates have also changed in the varied state then the *vis viva* would have to increase from the work δA that is done by that coordinate change with no additional supply of energy. The total increase in *vis viva* δL is thus equal to the *vis viva* $\delta_1 Q$ that is supplied from the outside plus the δA that is obtained by doing work. One thus has:

$$\delta_1 Q = \delta L - \delta A. \tag{6}$$

From equation (4), one has $\delta L = \delta(E - V)$. In order to determine δA, we would like to always arrange that the variation implies that we consider the rapidly-varying variables as not being capable of variation; i.e., we would always like to compare the original state of a system with the varied state of a system for which the rapidly-varying coordinates have precisely the same value. If the s are not true coordinates, but merely parameters that enter into the force function V, then any varied state will be compared to an unvaried state in which all coordinates have the same values. One will then have $\delta A = 0$, and the energy that is supplied by each system will have the value:

$$\delta_1 Q = \delta L = \delta(E - V).$$

Since these quantities possess the same value for all dN systems, $d\delta Q = dN \cdot \delta(E - V)$, and the energy that is supplied by all N systems will be:

$$\delta Q = \int dN \cdot \delta(E - V)\,.$$

By contrast, if true coordinates are also present among the s that determine the spatial position of the system components, and therefore they are also present in the coefficients μ, then the coordinates p will indeed have the same values in the varied state as in the unvaried one that they are compared to, but not the coordinates s. Work will then be performed by varying the last coordinates, which will consist of two parts:

1) Ones that are exerted by the forces that are determined by the force function V; the increase in the *vis viva* of the system that they produce will be:

$$-\sum_{k=1}^{a} \frac{\partial V}{\partial s_k} \cdot \delta s_k\,,$$

and

2) Ones that are exerted by the *Lagrange* forces, which insure that the coordinates s will stay constant. The latter work yields the *vis viva:*

$$\sum_{k=1}^{a}\left(\frac{\partial V}{\partial s_k}+\frac{\partial L}{\partial s_k}\right)\delta s_k = \sum_{k=1}^{a}\left(\frac{\partial V}{\partial s_k}+\sum_{h=1}^{b}\frac{q_h^2}{2}\cdot\frac{\partial \mu_h}{\partial s_k}\right)\delta s_k\,,$$

since the *Lagrange* force that acts against the growth of the s_k possesses the value $-\frac{\partial V}{\partial s_k}-\frac{\partial L}{\partial s_k}$. The total value of δA is then:

$$\sum_{k=1}^{a}\sum_{h=1}^{b}\frac{q_h^2}{2}\cdot\frac{\partial\mu_h}{\partial s_k}\cdot\delta s_k = \sum_{h=1}^{b}\frac{q_h^2}{2}\cdot\delta s_h,$$

if δ means the total increase that arises from the slow variation of the *s* and the *E* while the *p* are kept constant. Therefore, one will have:

$$\delta_1 Q = \delta(E - V) - \delta A = \delta(E - V) - \sum_{h=1}^{b}\frac{q_h^2}{2}\cdot\delta s_h.$$

If we would like to determine $d\delta Q$ from this then we would have to multiply by the value of $d\mathfrak{N}$ that is given by equation (3) and integrate the *q* over all possible values. Thus, one does not think of $E - V$ as a function of the *q*, and furthermore one thinks that:

$$\frac{\dfrac{\mu_h}{2}\iint\cdots\dfrac{q_h^2\cdot dq_1\cdot dq_2\cdots dq_{b-1}}{p_b'}}{\iint\cdots\dfrac{dq_1\cdot dq_2\cdots dq_{b-1}}{p_b'}}$$

is nothing but the mean value of $\mu_h q_h^2/2$, which is the same for all *q*, and is equal to $(E - V)/b$. (Cf., *Maxwell*, *loc. cit.*, pp. 558, formula 52.) One will then have:

$$d\delta Q = dN\cdot\left[\delta(E-V) - \frac{1}{b}(E-V)\sum_{h=1}^{b}\frac{\delta\mu_h}{\mu_h}\right].$$

The energy that is supplied by the totality of all systems is then:

$$\delta Q = \frac{2N}{b}\cdot\frac{\iint\cdots\left[\dfrac{b}{2}\delta(E-V) - \frac{1}{2}(E-V)\sum_{h=1}^{b}\dfrac{\delta\mu_h}{\mu_h}\right]\dfrac{(E-V)^{\frac{b}{2}-1}}{\sqrt{\mu_1\cdot\mu_2\cdots\mu_b}}dp_1\cdot dp_2\cdots dp_b}{\iint\cdots\dfrac{(E-V)^{\frac{b}{2}-1}}{\sqrt{\mu_1\cdot\mu_2\cdots\mu_b}}dp_1\cdot dp_2\cdots dp_b}$$

$$. \qquad = \frac{2N}{b}\cdot\frac{\delta\iint\cdots\dfrac{(E-V)^{\frac{b}{2}-1}}{\sqrt{\mu_1\cdot\mu_2\cdots\mu_b}}dp_1\cdot dp_2\cdots dp_b}{\iint\cdots\dfrac{(E-V)^{\frac{b}{2}-1}}{\sqrt{\mu_1\cdot\mu_2\cdots\mu_b}}dp_1\cdot dp_2\cdots dp_b}.$$

A possible variation of the limits produces no variation of the integral thus-determined, since the function under the integral sign vanishes at the limits, where it is not at all capable of variation. When certain variables go back to themselves, such as angles that increase by 2π, a variation of the limits does not actually exist, or one can say that the terms that arise by varying the upper and lower limits will cancel. Since the *vis viva* of all N systems combined possesses the value:

$$T = N \cdot \frac{\iint \cdots \frac{(E-V)^{\frac{b}{2}}}{\sqrt{\mu_1 \cdot \mu_2 \cdots \mu_b}} dp_1 \cdot dp_2 \cdots dp_b}{\iint \cdots \frac{(E-V)^{\frac{b}{2}-1}}{\sqrt{\mu_1 \cdot \mu_2 \cdots \mu_b}} dp_1 \cdot dp_2 \cdots dp_b},$$

one can also write:

$$\frac{\delta Q}{T} = \frac{2}{b} \delta \ln \iint \cdots \frac{(E-V)^{\frac{b}{2}}}{\sqrt{\mu_1 \cdot \mu_2 \cdots \mu_b}} dp_1 \cdot dp_2 \cdots dp_b \, ,$$

with which, the formula to be proved is presented in full generality. If one of the systems moves during a very long time t, and if δt is the increment in time t, during which the coordinates lie between the limits (1), then one will have:

$$dt = t \cdot \frac{\frac{(E-V)^{\frac{b}{2}-1}}{\sqrt{\mu_1 \cdot \mu_2 \cdots \mu_b}} dp_1 \cdot dp_2 \cdots dp_b}{\iint \cdots \frac{(E-V)^{\frac{b}{2}-1}}{\sqrt{\mu_1 \cdot \mu_2 \cdots \mu_b}} dp_1 \cdot dp_2 \cdots dp_b}.$$

Thus, if everything depends upon a single variable p that again assumes the same value after a finite time interval t (viz., the period of oscillation) then one will have:

$$t = \int \frac{dp}{2\sqrt{\mu}\sqrt{E-V}}, \quad \delta Q = 2T \, \delta \ln (T \cdot t).$$

Two masses m and μ that move in a circle with slowly-varying distances r and ρ from two fixed centers with the likewise slowly-varying angular velocities w and ω can serve to make this concrete. Here, one has $r = s_1$, $\rho = s_2$, $w = p_1'$, $\omega = p_2'$. N point-pairs must be present, for which all possible pairs of values for w and ω can occur for which:

$$\frac{mr^2w^2}{2} + \frac{\mu\rho^2\omega^2}{2}$$

has the required value E of total energy. Naturally, the condition that the properties of each individual point-pair are independent of their initial conditions is therefore not fulfilled by this example, which is why the theorem to be proved here will be true for only the mean value over all point-pairs, but not the values of the individual point-pairs themselves.

Graz, September 1885.