R. Clausius

On a mechanical law applicable to heat

(presented at the Niederrheinische Gesellschaft für Natur- und Heilkunde

on 13 June 1870 by the author)

Translation: Falk H. Koenemann, 2007[1]

To be quoted as: Clausius R (1870) Über einen auf die Wärme anwendbaren mechanischen Satz. Poggendorffs Annalen **141**, 124-130

In an essay from 1862 on the mechanical theory of heat (Clausius 1862, n.d.) I proposed a law which is in its simplest form: *the effective power of heat is proportional to the absolute temperature*. In connnection with the law of the equivalence of heat and work I deduced a number of conclusions on the behavior of bodies [materials] to heat. Since the law of the equivalence of heat and work can be reduced to a simple mechanical law, i.e. the law of the equivalence of kinetic energy and mechanical work, I was always convinced that there must be a mechanical law in which the law on the change of the effective power of heat with temperature might find its explanation. This law I believe I can now communicate.

Assume a system of material points[2] which are in stationary motion. By stationary motion I imply a motion by which the points do not move far away from their original position, and the velocities do not change continuously in one sense, but the positions of the points and the velocities vary only within limits. Examples are all periodic motions like the revolutions of the planets about the Sun, or vibrations of elastic bodies, but also irregular motions as they are assigned to atoms and molecules of a material in order to explain its heat.

Let m^i (i = 1, … n) be the material points, x^i_j (j = 1, 2, 3) their Cartesian coordinates at time t, and f^i_j the force components acting on them. [Superscripts refer to particles, subscripts to coordinates.] Then we sum:

$$\frac{m^i}{2}\left(e_j \frac{dx^i_j}{dt}\right)^2 \qquad [1]$$

for which we can write

$$\frac{m^i}{2}\left(e_j v^i_j\right)^2 \qquad [2]$$

if $\mathbf{v}^i$ are the velocities of the points m^i; the sum is known as the *living force* [kinetic energy] of the system. [**e** is a metric vector.] Furthermore, we form the expression

$$-\frac{f^i_j x^i_j}{2} \qquad [3]$$

[1] Italics by original author (Rudolf Julius Emanuel Clausius, 1822-1888). Text in [brackets] added by translator. Obsolete terminology is once accompanied by modern equivalent in brackets, whence modern terminology is used only. Equations were originally not numbered. Mathematics in modern notation. – Clausius' style of writing was very flowery and repetitive. It appeared proper to be more succinct, for the sake of understanding. FKoe

[2] [Clausius makes the assumption that a kinetic system contains n discrete bodies which are spatially extended, and which are allowed to move in freespace. A discrete body is one that can be enveloped by a closed surface that does not pass through mass. Such bodies can be thought to be reduced to mass points in the sense that their volume is zero, but their finite mass is concentrated in a point, their center of mass.]

which is strongly dependent on the forces acting within the system. Its magnitude is proportional to $|\mathbf{f}|$ if the latter were to change in one direction only. The mean over time during a stationary motion is now called the *virial* [average internal kinetic energy] of a system, after the Latin word *vis* = force[3].

In contrast to the mean over time, the internal kinetic energy at time *t* is marked by a bar,

$$\frac{m^i}{2}\overline{\left(e_j v_j^i\right)^2} = -\frac{\overline{f_j^i x_j^i}}{2}. \qquad [4]$$

The magnitude of the average kinetic energy is a simple matter. Consider the mass points m_1 and m_2 which are separated by distance *r*. Let the [electromagnetic] forces $\varphi(r)$ which they exert upon one another be attractive (positive) and repulsive (negative), and let them be some function of distance. Thus we have

$$f_1^{\,1} x_1^1 + f_1^{\,2} x_1^2 = \varphi(r)\frac{x_1^2 - x_1^1}{r} x_1^1 + \varphi(r)\frac{x_1^1 - x_1^2}{r} x_1^2 = -\varphi(r)\frac{(x_1^2 - x_1^1)^2}{r}; \qquad [5]$$

the sum over all coordinates is then

$$-\frac{1}{2}\left(f_j^{\,1} x_j^1 + f_j^{\,2} x_j^2\right) = \frac{1}{2} r\varphi(r); \qquad [6]$$

if the sum is taken over all mass points ($n = i$),

$$-\frac{1}{2} f_j^{\,i} x_j^i = \frac{1}{2}\sum\nolimits_i r\varphi(r), \qquad [7]$$

such that all dual mass point combinations are considered. It follows for the average internal kinetic energy

$$\frac{1}{2}\sum \overline{r\varphi(r)}. \qquad [8]$$

The analogy between this expression and the one for the calculation of the work done during the motion is obvious. If the function $\Phi(r)$ is introduced where

$$\Phi(r) = \int \varphi(r)\, dr, \qquad [9]$$

we arrive at the well-known equation

$$-f_j^{\,i} dx_j^i = d\sum \Phi(r) \qquad [10]$$

If the magnitudes of the attractive and repulsive forces are inversely proportional to the distance, the sum $\sum \Phi(r)$ is the *potential* of the system of points upon itself. It might be useful to have a convenient name for this term[4], independent of the particular form of the law that controls the forces, provided they can be given in differential form as a function of the coordinates. The term whose differential represents the negative work is therefore named the *ergal* of the system [work done in the system], after the Greek εργον = work. The equivalence

[3] [Lat. *vis* is ambiguous in modern understanding. *Vis* alone is force (Newton) whereas *vis viva* and *vis mortua* are the kinetic and potential energy, respectively (Joule). The modern names for the energetic terms were coined in 1787 by Thomas Young, but the common convention changed only late in the 19th century.]

[4] The expression *force function* is somewhat inconvenient and has the disadvantage that it is already in use for a different term which relates to the one in discussion here in a similar way as the potential function to the potential.

of kinetic energy and work thus finds a simple form. To demonstrate the analogy of this law and the one given above I present them here together:

1. The sum of kinetic energy and ergal is constant.
2. The average kinetic energy is identical to the virial.

In order to apply this law on heat, we consider a body as a system of moving mass points. The forces acting on them can be divided into two groups: the (positive and negative) forces exerted by the particles upon one another, and the forces that are exerted from outside upon the interior. Thus we can divide the average kinetic energy into two parts, one of which is due to the internal forces (internal virial), and one is due to the external forces (external virial).

Provided the internal forces are all central forces, the internal virial [average internal kinetic energy] is given by eqn.3. In case of a body in which an infinite number of atoms move in a way that is in principle irregular, but similar such that all possible motion phases are existent simultaneously, it is not necessary to consider all $r\varphi(r)$ for every pair of atoms. Instead, the $r\varphi(r)$ can be taken at time t since the sum will not change notably in the course of the various motions. The internal virial thus has the form (cf. eqn.7)

$$\frac{1}{2}\sum r\varphi(r)\,. \qquad [11]$$

The external virial is very simple if the external pressure is isotropic. If p is pressure and v is volume, it is just

$$\frac{3}{2}pv\,. \qquad [12]$$

If the internal kinetic energy is equated with heat h, we get the following equation.

$$h = \frac{1}{2}\sum r\varphi(r) + \frac{3}{2}pv\,. \qquad [13]$$

We are left to prove the law that relates kinetic energy to virial.

The equations governing the motion of a material point are:

$$m\frac{d^2 x_j}{dt^2} = f_j\,. \qquad [14]$$

However,

$$\frac{d^2(x^2)}{dt^2} = 2\frac{d}{dt}\left(x\frac{dx}{dt}\right) = 2\left(\frac{dx}{dt}\right)^2 + 2x\frac{d^2x}{dt^2}\,; \qquad [15]$$

rearrange,

$$2\left(\frac{dx}{dt}\right)^2 = -2x\frac{d^2x}{dt^2} + \frac{d^2(x^2)}{dt^2}\,. \qquad [16]$$

Multiply by $\frac{m}{4}$, replace $m\frac{d^2x_j}{dt^2}$ by f_j, arrive at

$$\frac{m}{2}\left(\frac{dx_j}{dt}\right)^2 = -\frac{1}{2}f_j x_j + \frac{m}{4}\cdot\frac{d^2\left((x_j)^2\right)}{dt^2}\,. \qquad \text{[no sum on } j \text{ in eqns.17 to 20]} \qquad [17]$$

Integrate over t and take average over time, get

$$\frac{m}{2t}\int_0^t\left(\frac{dx_j}{dt}\right)^2 dt = -\frac{1}{2t}\int_0^t f_j x_j dt + \frac{m}{4t}\left[\frac{d\left(\left(x_j\right)^2\right)}{dt} - \left(\frac{d\left(\left(x_j\right)^2\right)}{dt}\right)_0\right], \qquad [18]$$

where $\left(\frac{d\left(d\left(x_j\right)^2\right)}{dt}\right)_0$ indicates the initial value of $\frac{d\left(\left(x_j\right)^2\right)}{dt}$.

The formulas in this equation,

$$\frac{1}{t}\int_0^t\left(\frac{dx_j}{dt}\right)^2 dt \quad \text{and} \quad \frac{1}{t}\int_0^t f_j x_j dt, \qquad [19]$$

represent the mean values of $\left(\frac{dx}{dt}\right)^2$ and $f_j x_j$ which were above indicated by $\overline{\left(\frac{dx}{dt}\right)^2}$ and $\overline{f_j x_j}$ if t is sufficiently large so that the mean values are stable.

In case of a periodical motion the last term in eqn.18 is zero at the end of every period. In case of an irregular motion the term in brackets cannot grow indefinitely, but must vary within limits; since t in the denominator grows continuously, the term in brackets must approach zero with time. Hence we can ignore this term, and we get

$$\frac{m}{2}\overline{\left(\frac{dx}{dt}\right)^2} = -\frac{1}{2}\overline{f_j x_j}. \qquad \text{[no sum on } j \text{ in eqns.17 to 20]} \qquad [20]$$

Since the same holds for all coordinates we get

$$\frac{m}{2}\overline{\left(\frac{dx_j}{dt}\frac{dx_j}{dt}\right)} = -\frac{1}{2}\overline{f_j x_j} \qquad [21]$$

or

$$\frac{m}{2}\overline{v^2} = -\frac{1}{2}\overline{f_j x_j}, \qquad [22]$$

and for a system of an arbitrary number of points

$$\sum_i \frac{m}{2}\overline{v^2} = -\frac{1}{2}\sum_i \overline{f_j x_j} \qquad [23]$$

Thus the law is proven.

References

Clausius R (1862) Poggendorffs Annalen **116**, 73
Clausius R (no date) Abhandlungen über die mechanische Wärmetheorie, Vol.1, p.242