

TEMPERATURE AS A THEORETICAL CONCEPT

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In the spirit of Einstein's critical analysis of the notions in physics, we have analysed the concept of temperature in the series of theoretical papers. Among those papers Einstein's works in thermodynamics are important for two reasons. From one side, he developed, to a certain extent, independently of Gibbs, the theory which we now call statistical thermodynamics. From the other side, in explaining the series of phenomena (black-body radiation, specific heat of crystals, the behaviour of quantum ideal gas) Einstein enlarged the area of applicability of Boltzmann statistical physics.

In comparison with other basic physical quantities the temperature is a specific one. Its specificity comes from the fact that for its measurements it is not enough to choose the unit but it is necessary to choose fix points and to establish the scale. The establishment of thermodynamical equilibrium between two bodies is also necessary.

The modern standard thermometer is a gas thermometer (most often helium one) whereas the temperature scale is determined¹ by the relation

$$T = 273,16^{\circ}\text{K} \frac{p}{p_0} \quad V = \text{const.} \quad (1)$$

p_0 is a pressure of the ideal gas at temperature $T_0 = 273,16^{\circ}\text{K}$.

From (1) it is evident that the dependence of other physical quantities of an ideal gas on temperature can be derived if one finds the relation between pressure and the quantity which is studied.

On the basis of the laws of mechanics and supposing that the atoms of the gas collide elastically with the walls of the container Boltzmann derived relation between total energy U of a gas, the pressure of a gas and the volume of a container

$$U = \frac{3}{2} pV \quad (2)$$

Combining (2) and (1) and the equation of state of a gas, Boltzmann found that energy per particle is proportional to temperature

$$U = \frac{3}{2} NkT \quad (3)$$

But, the most spectacular result of the Boltzmann gas theory² is a relation between entropy and probability which reads

$$S = k \log P - KN \cdot \log N + C \quad (4)$$

N is the number of particles of a gas, C is an unknown constant and P is given by

$$\log P = \log N! - \iiint f(xyzv_x v_y v_z) \cdot \log (xyzv_x v_y v_z) dx dy dz dv_x dv_y dv_z \quad (5)$$

where f is the equilibrium distribution function of particles in six - dimensional phase space.

Boltzmann found also that the Lagrange multiplier ϵ associated with the energy condition, which appears in the maximization of entropy as a functional of distribution function, has the property

$$\frac{\partial S}{\partial U} = \beta k \quad (6)$$

Since, from thermodynamics one has

$$\frac{\partial S}{\partial U} = \frac{1}{T} \quad (7)$$

it follows

$$k\epsilon = \frac{1}{T} \quad (8)$$

In deriving the relations (4) and (8) Boltzmann used the thermodynamic

definition of entropy

$$dS = \frac{dQ}{T} \quad (9)$$

the equation of state of the ideal gas and the relation (2).

Taking into account all those facts the relation (4) can not be regarded as generally valid. In other words, the application of this relation to other systems should be in inductive rather than in deductive sense.

But, in the history of physics from Boltzmann to our days, the relation (4) and the subsequent procedure has been applied deductively most often than inductively.

Along this line of thought the work of Planck³ and Bose⁴, dealing with the dependence of the spectral density of the black-body radiation, is mostly known.

Einstein has developed the theory of quantum ideal gas⁵ on the basis of the relation (4), but changing the dependence of P on f . This theory has been successfully applied to the theory of superconductivity and superfluidity. Einstein has applied also this relation to the theory of specific heat of crystals⁶.

The generalised Boltzmann procedure has been applied successfully whenever the macroscopic system can be regarded as a set of noninteracting "particles".

The dependence of physical quantities on temperature, of any macroscopic system of interacting particles, has been usually derived by studying the ensemble of replicas of a physical system which is in contact with a thermostat. This idea has been developed, to a certain extent, by Einstein⁷, independently of Gibbs⁸.

Gibbs and Einstein have studied the systems for which the energy is the only integral of motion. The imagined ensemble of replicas of a physical system is identified with a set of noninteracting systems.

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The states of the system are described by a point in the space of variables $\vec{q}_1 \dots \vec{q}_N \vec{p}_1 \dots \vec{p}_N$ - called phase space . With this ensemble the probability density is associated

$$\rho = \exp [- E/\theta] / \int \exp [- E/\theta] d\Gamma \quad (10)$$

E is the energy of the system, which is treated as a random quantity; θ is a parameter.

The average energy - \bar{E} , of the ensemble, is identified with the thermodynamic energy U .

One shows that the parameter θ has the property that for two systems Σ_1 and Σ_2 which are in thermodynamic equilibrium, the equality $\theta_1 = \theta_2$ is satisfied. This is the property of temperature in thermodynamics.

Whereas Einstein interrupted his idea at this point, Gibbs prolonged his thought as follows.

At first, Gibbs introduced the following assumptions:

The energy of the system is a sum of kinetic energy E_k , being the function of phase variable $\vec{p}_1 \dots \vec{p}_N$ and of potential energy E_p , being the function of particle coordinates $\vec{q}_1 \dots \vec{q}_N$ and of coordinates $a_1, a_2 \dots$ of some external bodies.

The forces $A_1, A_2 \dots$ are associated with the external coordinates $a_1, a_2 \dots$ through the relation

$$\frac{\partial E}{\partial a_i} = \frac{\partial E_p}{\partial a_i} = - A_i \quad i = 1, 2, \dots, p \quad (11)$$

The external coordinates a_i have the same values for all replicas in the ensemble.

The mean value of the force A_i is identified with the macroscopic quantity which is associated with the changes of the coordinate a_i

$$\bar{A}_i = - \int \frac{\partial E}{\partial a_i} \exp [- E/\theta] d\Gamma / \int \exp [- E/\theta] d\Gamma \quad (12)$$

Gibbs showed that the function ψ defined by

$$\exp [-\psi/\theta] = \int \exp [-E/\theta] d\Gamma \quad (13)$$

is identical with the free energy in thermodynamics whereas the function \bar{S}

$$\bar{S} = \frac{\bar{E} - \psi}{\theta} \quad (14)$$

is identical with the thermodynamical entropy. This statement is based on the fact that the functions S , E , and A_i satisfy the differential equation

$$\theta d\bar{S} = d\bar{E} + \bar{A}_1 da_1 + \bar{A}_2 da_2 \dots \quad (15)$$

which is analogous to the second law of thermodynamics.

$$T dS = dU + A_1^t da_1 + A_2^t da_2 \dots \quad (16)$$

Gibbs derived also the equality

$$\bar{A}_k = - \frac{\partial \psi(\theta, a_1, \dots, a_p)}{\partial a_k} \quad k = 1, \dots, p \quad (17)$$

We found that in the derivations of the differential equation (15) and of the equality (17) one assumption has been used, but has never been stated explicitly by Gibbs. The assumption is that the limits of integration over phase space do not depend on external coordinate a_k ($k=1, \dots, p$). In applying those equalities, it is important to know that this assumption is incorporated in the whole procedure.

The simplest check of this general theory can be obtained by evaluating the definition expressions in the case of an ideal gas enclosed in a box of volume V . In the language of Gibbs, V is the external coordinate, whereas the pressure p is the associated force.

A) Dealing with the ideal gas Einstein and Gibbs used only the part of the procedure. By calculating \bar{E} Gibbs and Einstein

found

$$\bar{E} = N \frac{3\theta}{2} \quad (18)$$

Then using Boltzmann relation (2) between pressure, volume and the total energy and identifying U with \bar{E} the relation

$$\bar{P} = \frac{N\theta}{V} \quad (19)$$

is established. From this relation it has been concluded that θ is proportional to temperature. But, the complete application of the general procedure should contain the calculation of pressure \bar{P} from the definition expression (12).

B) In Fowler's approach the gas is supposed to be in a cylinder of length y and of cross section A ($V = yA$). The total energy is the sum of the total kinetic energy and of the interaction energy of all molecules with the wall of the cylinder. The latter is written in the form

$$\begin{aligned} \mathcal{E}_p(\vec{q}_1, \dots, \vec{q}_N, y) &= \sum_i e_{pi}(\vec{q}_i, y) \\ e_{pi}(\vec{q}_i, y) &= \frac{D}{(y - q_{xi})^s} \end{aligned} \quad (20)$$

D and s are unknown parameters.

The generalised force associated with the external coordinate y is calculated applying Eq. (17). In the limit $D \rightarrow 0$, Fowler found that pressure \bar{p} satisfies (19).

But, we want to make a remark here. The limits of integration in Fowler's free energy depend on the "external" coordinate - y and it is useful to investigate whether the equation (2133) in Ref. 9 is applicable. In order to answer this question one has to investigate whether the equality

$$\frac{\partial}{\partial y} \int_0^y \exp[-D/\theta(y-x)^s] dx = \int_0^y \frac{\partial}{\partial y} \exp[-D/\theta(y-x)^s] dx \quad (21)$$

is valid.

From the equality

$$\frac{\partial}{\partial y} \int_0^y \exp \left[-D/\theta(y-x)^5 \right] dx = \int_0^y \exp \left[-D/\theta(y-x)^5 \right] dx + \exp \left[-D/\theta(y-x)^5 \right] / y=x \quad (22)$$

it follows that Eq. (21) is satisfied. We see that due to the special form of the electron-wall interaction, the expressions $-\frac{\partial \bar{E}}{\partial V}$ and $-\frac{\partial \bar{U}}{\partial V}$ are identical despite the fact that the limits of integration over phase space depend on volume.

C) In evaluating pressure, Khinchin considers¹⁰ the gas in the cube of the edge $a = \sqrt[3]{V}$ and writes the energy as a sum of kinetic energy and potential energy. Potential energy equals zero inside the box and is infinite outside the box.

On the basis of Eq. (17) Khinchin finds that pressure, volume and parameter θ satisfy the relation (19). If one tries for the Khinchin energy of a gas in a box to calculate pressure, from the definition expression (12), one concludes that it is not possible because the derivative of Khinchin's energy over volume V does not exist.

D) The authors of most textbooks¹¹⁻¹⁵ identify the energy of a gas with the total kinetic energy ($E_p(\vec{q}_1, \dots, \vec{q}_N, V) = 0$). On the basis of Eq. (17) they get the equation (19). On the other hand, it is easy to see that since $\frac{\partial E_p}{\partial V} = 0$, the definition expression (12) for pressure gives $\bar{p} = 0$.

The difference arises because the equality

$$\frac{\partial}{\partial a} \int_0^a \exp \left[-e_p(q, a)/\theta \right] dq_x = \int_0^a \frac{\partial}{\partial a} \exp \left[-e_p(\vec{q}, a)/\theta \right] dq_x + \exp \left[-e_p(\vec{q}, a)/\theta \right] / q_x = a \quad (22)$$

has not been respected. When $e_p(\vec{q}, a) = 0$, the last equality takes the form

$$\frac{\partial}{\partial a} \int_0^a dq_x = 0 + 1 \quad (23)$$

So, despite the fact that $\frac{\partial e_p(\vec{q}, a)}{\partial a}$ equals zero, the derivative

$\frac{\partial}{\partial a} \int_0^a dq_x \exp[-e_p/\theta]$ is different from zero. Consequently, pressure calculated from $-\frac{\partial \bar{E}}{\partial V}$ is different from zero.

E) Wergeland¹⁶ studied the ideal gas enclosed in a sphere of radius R . The potential energy is written in the form

$$E_p = \sum_i e_p(\vec{q}_i, R); \quad e_p(\vec{q}_i, R) = \begin{cases} C(q_i - R) & q_i > R \\ 0 & q_i < R \end{cases} \quad (24)$$

On the basis of Eq. (17) Wergeland also derived Eq. (19). But, if one goes back to the definition equation (12) one concludes that it is difficult to understand the physical meaning of this result, because $-\frac{\partial E_p}{\partial R} = 0$ inside the sphere and $-\frac{\partial E_p}{\partial R} = NC$ outside the sphere. Namely, pressure whose mean value is calculated, is zero inside the container.

Wergeland¹⁶, Münster¹⁷ and Klein¹⁸ have studied the difficulties which one meets in calculating pressure fluctuations. In our opinion those difficulties are the same as those which we found in calculating pressure from the definition expression. The source of the difficulties lies in the assumption that energy depends at the same time on phase variables and on volume. As it is clear from the above exposition, different suppositions have been made about the form of this dependence.

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