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On the Dependence of the Internal Energy of a Solid on the Rate of Change of Temperature

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1°. At the present time, in the thermodynamics of irreversible processes it is usually assumed that the nonequilibrium values of thermodynamic functions depend on the same set of parameters as under thermodynamic equilibrium ([1]). At the same time, Prigogine showed ([1]) that, when the nonequilibrium of a process is strongly pronounced, the nonequilibrium thermodynamic functions may depend explicitly on gradients of the system parameters, for example on temperature gradients. In this connection there arises the question of finding the complete set of parameters that determine a nonequilibrium process and the values of thermodynamic functions.

Since at present a reliable investigation of nonequilibrium processes in solids by the methods of statistical physics is scarcely possible, there remains only one possibility—the introduction of phenomenological working hypotheses and their verification in macroscopic experiments. As a first step it makes sense to consider the question of a possible dependence of the internal energy of a solid on the rate of change of temperature.

The internal energy V of a body and its temperature T can, in a number of cases, be measured independently, which facilitates a direct experimental investigation of the relations between them.

2°. With the additional assumption of linearity of the relations between nonequilibrium thermodynamic functions, let us consider the alternatives A^0 and B^0.

$$\begin{aligned} \mathrm{A}^0.\quad & V = cmT + \text{const}, \\ & \sigma_{ij} = 0; \\ \mathrm{B}^0.\quad & V = cmT + bm\dot{T} + \text{const}, \end{aligned} \tag{1}$$

where V is the internal energy of the specimen, T its current temperature, m the mass, c the specific heat, b a certain coefficient, and σ_{ij} the stress tensor. A dot denotes differentiation with respect to time. It is assumed that V is

Fig. 1

Figure 1: Fig. 1

distributed uniformly over the volume and that the temperature is constant over the volume.

Hypothesis A^0 is generally accepted; hypothesis B^0 takes into account the possibility of a dependence of V on $\dot{T}$. Let us consider the following process (Fig. 1).

Let, during a small time interval $0 < t < \tau$, an energy ΔV be supplied to the body by means of a heat pulse that does not disturb the uniformity of the distribution of V over the volume. The change in the internal energy of the body is determined by the relation

$$dV = dQ \qquad (dA^e = 0), \tag{2}$$

where dQ and dA^e are the heat received by the body during the time dt, and the work performed by external forces on the body during the same time. For $t > \tau$ (the action of the heat pulse has ended), $V = \text{const}$. How will the temperature of the body change in this process? In case A^0, T will reach at $t = \tau$ its limiting value $T_\text{k} = \Delta V/cm$ and will not change further. In case B^0

at the instant $t = \tau$ the temperature will be equal to some $T_1 \neq T_\text{k}$. For $t > \tau$ the temperature will change according to the equation

$$cmT + bm\, dT/dt' = \text{const}, \qquad T(0) = T_1, \tag{3}$$

if the origin of time t' coincides with the instant $t = \tau$. The solution of this equation has the form

$$T(t') = (T_1 - T_\text{k})e^{-\frac{c}{b}t'} + T_\text{k}. \tag{4}$$

Thus, if in case A^0, for $t > \tau$, $T = T_\text{k} = \text{const}$, then in case B^0, for $t > \tau$, T changes according to (4). For $t < \tau$ the graphs of the functions $V(t)$ and $T(t)$ coincide (to within scale) in case A^0 and are shifted relative to one another in time in case B^0.

Thus, by realizing the process considered in an experiment and independently measuring $V(t)$ and $T(t)$, one can reveal the dependence of V on $\dot{T}$, if it exists.

Fig. 1

3°. The arrangement of the experimental setup is shown in Fig. 2. The specimen 1 consists of two copper rods 1.5–2.75 mm in diameter and 10–75 cm long, made from a single piece of copper wire that had been preliminarily stretched

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

beyond the elastic limit. The rods are placed in a longitudinal immobile porcelain tube 2, along which they can move with negligible friction. A short tie rod 3 is soldered to the right ends of the rods; at the end of it is attached a blackened mica plate 4. It partially covers the opening of the photoelement 5, illuminated by the lamp 6. The opposite ends of the specimen are rigidly fixed against displacement in a Plexiglas clamp 7. Current leads from these ends of the rods go to an alternating-current source 8 of frequency 50 Hz: one end is connected to one of the phases of a 380 V mains supply (one phase 220 V), and the other to ground. The circuit contains a switch 9 and a fusible resistance 10, made of copper wire 0.20–0.25 mm in diameter and 3–6 cm long. From the end 11 of one of the rods a voltage is taken, which is fed to input X of an EO-7 oscillograph (12 in the drawing), and the signal from the photoelement is fed to input Y of the same oscillograph. The power supplies of the measuring instruments and the time-mark sensor are not shown in the figure.

Fig. 2

The setup described operates as follows. When switch 9 is closed, a powerful ($\approx$ 10,000 A) electric current arises in the circuit. Resistance 10 burns out and opens the circuit. The diameter of wire 10 is chosen so that it burns out in approximately 0.01 sec (one half-cycle of the current).

The electric pulse obtained heats specimen 1 uniformly over its length and cross section by approximately 5°; the specimen elongates, and plate 4 covers part of the aperture of photoelement 5, changing the luminous flux. The change in electromotive force obtained in the photoelement, proportional to the elongation of the specimen, is fed to the Y input of oscilloscope 12. Thus, along the X axis of the screen of oscilloscope 12 the variable current in the circuit is plotted, and along the Y axis—the variable elongation of the specimen. The time-marker generator ZG-10 produces time marks—dots (beam-brightness modulation frequency 2000 or 4000 Hz), with the aid of which, on one and the same oscillogram, one can construct plots of two functions $i(t)$ and $\Delta l(t)$, where i is the current, Δl is the elongation of the specimen, and t is time.

Fig. 3

4°. The processing of the measurement results reduces to the following. From the measured current through the specimen, its internal energy is calculated by numerical integration (the Joule–Lenz law)

$$V(t) = Q(t) = A\int_0^t i^2(\tau)\,d\tau. \tag{5}$$

In doing this, it is taken into account that the resistance of the specimen is unchanged (the temperature change is small), the kinetic energy of the macroscopic motion of the specimen is negligible (it is easily estimated by taking into account the velocity of motion $\dot{l}$ of the end of the specimen), wave processes during expansion of the specimen may be neglected (the period of the specimen' s natural oscillations is $7\cdot10^{-6}$–$5\cdot10^{-4}$ sec, i.e., much less than the duration of the electric pulse), and heat exchange with the surrounding medium may be neglected.

The temperature of the specimen is calculated from the relation

$$\Delta l(t) = \alpha l_0 \Delta T(t) \quad \text{for } \sigma_{ij} = 0, \tag{6}$$

where l_0 is the initial length of the specimen, and α is the coefficient of linear expansion, which is taken to be constant. This relation is used in thermoelasticity for calculating very rapid processes, up to wave processes ([2]).

The results of processing one of the oscillograms are presented in Fig. 3. For convenience of comparison, the plots of the functions $T(t)$, $V(t)$ are presented on one scale. The time shift between the plots of these functions is 0.0010–0.0015 sec for all specimens. At the time a, when half of the total pulse energy has been imparted to the specimen, its temperature is only 25–30% of the final value. At the time d, when the supply of energy has practically ceased, the temperature change continues, and the corresponding instantaneous value of T is 80–85% of the final value.

Thus, the experimental data indicate the existence of a dependence of the internal energy V of a solid on the rate of change of temperature T.

An estimate of the order of magnitude of the coefficient b (see (1)) shows that

$$b/c \approx 0.001 \text{ sec.}$$

5°. In describing the theory of the experiment it was assumed that the distribution of energy over the mass of the specimen is homogeneous. However, the homogeneity of this distribution may be disturbed by: the finite rate of change of the electric current, the finite rate of exchange of energy between the electrons and the lattice, and the skin effect. The characteristic time of existence of inhomogeneities due to the first two causes is of the order of 10^{-8}–10^{-9} sec. The skin effect for copper wires of diameter 1 mm manifests itself at a frequency of several

kilohertz [(3)], therefore under the experimental conditions (a half-wave at a frequency of 50 Hz) the skin effect can be neglected. Thus, uniformity of the distribution of V over the specimen is ensured under the experimental conditions.

With regard to relation (6), which was substantially used in processing the experimental data, the following remark must be made. Since the question of the dependence $V(\dot{T})$ is being discussed, the question should also arise of a possible dependence of Δl on $\dot{T}$. We shall show that using, instead of (6), a relation of the type

$$\Delta l(t) = \alpha l_0 \Delta T + \beta \Delta \dot{T} \tag{7}$$

does not remove the established dependence $V(\dot{T})$. We shall prove this by contradiction. Let $V = V(T)$, but not $V(T, \dot{T})$. Then for $t \geq \tau$ (after the end of the pulse) $V =$ const, and hence $T =$ const. But then, according to (7), $\Delta l =$ const as well. However, as the experiment shows, elongation of the specimen continues at $V =$ const. Thus, using relation (7) instead of (6) also leads to a dependence of V on $\dot{T}$. However, the law of variation of $T(t)$ for $t \leq \tau$ will then already differ from that presented in Fig. 3.

6°. When specimens in the form of short (10–20 cm) thin-walled (wall thickness 0.25 mm) tubes of diameter 5 mm were used, the setup scheme was partially changed. Instead of the function $\Delta l(t)$ at $\sigma_{ij} = 0$, an oscillogram $\Delta\sigma(t)$ at $\Delta l = 0$ was recorded, where $\Delta\sigma$ is the axial compression of the specimen. A barium titanate plate 1 mm thick (in some cases two plates) was used as the pressure transducer. In this case, when the specimen clamped between two fixed supports was heated by current, compressive forces arose in the specimen at constant length. The temperature change ΔT_k was less than 1°. Otherwise the scheme was analogous to that described. The results of this experiment proved identical to those obtained with the setup described in 3°–4°.

7°. It was assumed above that the nonequilibrium state of the specimen can be characterized by a single nonequilibrium parameter T, determined by (6) or (7). At the same time, it is known that in describing a number of nonequilibrium processes it is necessary to introduce several temperatures, assigning them to different subsystems (for example, the temperature of the lattice and of the set of nuclear spins). It is difficult to expect that, in the comparatively slow processes realized in the experiment described, the state of the specimen should be characterized not by one but by several temperatures of several subsystems. Nevertheless, such a possibility is in principle not excluded. If a more detailed study of this process shows that, to describe it, it is necessary to introduce several subsystems (for example, lattice and electrons) with different temperatures and to investigate the process of establishment of thermodynamic equilibrium between these subsystems, then the interpretation of the experimental results will have to be changed. In this interpretation, the experiment directly determines the relaxation time of the process of establishment of thermodynamic equilibrium between the subsystems, and this time τ has a magnitude on the order of 0.001 sec.

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Note: Figure translations are in progress. See original paper for figures.