SOVIET PHYSICS JETP VOLUME 17, NUMBER 5 NOVEMBER, 1963

ATTAINMENT OF NEGATIVE TEMPERATURES BY HEATING AND COOLING OF A SYSTEM

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Submitted to JETP editor October 19, 1962

J. Exptl. Theoret. Phys. (U.S.S.R.) **44**, 1742-1745 (May, 1963)

It is pointed out that because of differences in the relaxation times for various energy levels during establishment of thermodynamic equilibrium, rapid variation of the system temperature may create a negative temperature state for certain pairs of energy levels.

1. In quantum systems one can often find subsystems such that the establishment of equilibrium between them requires more time than the establishment of equilibrium within the subsystems themselves; radiative transitions between the subsystems are thereby possible. During a sufficiently rapid change in the thermodynamic state, equilibrium is established sufficiently rapidly within each subsystem, but the subsystems are not in equilibrium with one another. This can create a state of negative temperature with respect to transitions from the energy levels of one subsystem to those of another.

2. We shall consider a three-level system having different relaxation times between the levels 1, 2, 3 numbered from bottom to top.

If the probability of transitions from level 1 to level 3 is significantly greater than those for the transitions from level 1 to level 2 and from level 3 to level 2, then during a sharp rise in temperature thermal equilibrium is quickly established between levels 1 and 3, and for some time there will be no equilibrium between levels 1 and 2 and between levels 3 and 2. In this case a state of negative temperature can arise between levels 3 and 2. The same result can be effected by cooling the system, but with different relations between the transition probabilities. In this case we should have $w_{32} \gg w_{31}, w_{21}$ or $w_{21} \gg w_{31}, w_{32}$. In the first of these cases a negative temperature state arises between levels 1 and 2, in the second between 3 and 2.

In order to obtain more accurate quantitative relations we shall assume that the system is rapidly heated from temperature T_i to a temperature $T_f > T_i$. The change in population between the levels is described by the system of equations

$$dn_3/dt = -(w_{31} + w_{32})n_3 + w_{23}n_2 + w_{13}n_1 \tag{1}$$

$$dn_2/dt = -(w_{21} + w_{23})n_2 + w_{32}n_3 + w_{12}n_1;$$

$$n_1 + n_2 + n_3 = n_0, \tag{2}$$

where n_i is the population of the i-th energy level, and w_{ik} is the transition probability per unit time from level i to level k.

The possible changes in the population difference with time are shown in a qualitative way in the figure. (Relaxation processes are always aperiodic in nature.) A favorable change for obtaining a state of negative temperature is shown in the graph as a heavy line. Its distinguishing character is the existence of a positive maximum at $t_m > 0$. Hence a necessary and sufficient condition for the establishment of a negative temperature state is

$$\max(n_3 - n_2) = A(1 - a)e^{-\lambda_1 t_m}$$
$$+ B(1 - b)e^{-\lambda_2 t_m} + n_{30} - n_{20} > 0, \tag{3}$$

wherein

$$t_m = \frac{1}{\lambda_2 - \lambda_1} \ln\left[-\frac{B(1 - b)}{A(1 - a)} \frac{\lambda_2}{\lambda_1}\right] > 0. \tag{4}$$

In these formulas,

$$A = \frac{n_{20} - N_2 - (n_{30} - N_3)b}{b - a}, \qquad B = \frac{n_{20} - N_2 - (n_{30} - N_3)a}{a - b},$$

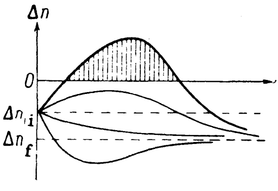
N_3, N_2, n_{30}, and n_{20} are the equilibrium values of the populations at the initial and final temperatures, respectively;

$$a = (\lambda_1 - \alpha)/\beta, \qquad b = (\lambda_2 - \alpha)/\beta, \qquad \alpha = w_{31} + w_{13} + w_{32},$$

$$\beta = w_{13} - w_{23}, \qquad \delta = w_{21} + w_{12} + w_{23}, \qquad \gamma = w_{12} - w_{32},$$

and λ_1 and λ_2 are the roots of the characteristic equation of the system (1).

Conditions (3) and (4) give us the necessary relations between T_i, T_f, and the transition probabilities w_{ik}. In particular, for $T_i \ll h\nu_{21}/k$ we



Change in population difference $\Delta n = n_3 - n_2$ with time. The shaded portion corresponds to negative temperature.

will have $N_2 \approx N_3 \approx 0$. Then (3) and (4) are equivalent to the simple relation

$$w_{12} < w_{13}. \tag{5}$$

The conditions (3) and (4) place a limit on the initial temperature, since for very large initial temperatures a negative temperature state cannot be produced for any relation between the transition probabilities. This comes about in case

$$N_3 + N_1 \leqslant 2N_2,$$

or

$$1 + \exp(h\nu_{31}/kT_i) \leqslant 2\exp(h\nu_{32}/kT_i). \tag{6}$$

One can also carry out a similar analysis for the case $T_i > T_f$, i.e., for rapid cooling of the system.

3. A mixture of para- and orthohydrogen will serve as a concrete example of such a system.

It is known[1] that, because of the Pauli principle, parahydrogen has only even rotational levels (rotational quantum number J even), and orthohydrogen has odd rotational levels (J odd). A transition involving a change in rotational energy $J \rightarrow J \pm 1$ must be accompanied by a change in molecular modification and therefore has a small probability.[2] Because of this, a mixture of ortho- and parahydrogen behaves like a two-component gas, and when the temperature is changed, thermal equilibrium with respect to the energy of the reciprocating motion and the internal energy of each component is fairly rapidly established, but equilibrium between the components is attained only after a sufficiently long time if no catalyst is present. Say we have ordinary hydrogen (ratio of ortho to para is 3:1). If we cool it in the presence of a catalyst to below 20°K, then it transforms to pure parahydrogen in the state $J = 0$. Upon subsequent heating without a catalyst the rotational levels with even values of J will become filled. The levels with odd J will remain empty, and a negative temperature state will have been created with respect to the transition

$$J^{\text{even}}_{\text{para}} \rightarrow J^{\text{odd}}_{\text{ortho}}. \tag{7}$$

Another example of a system permitting the realization of the proposed method is a system of symmetric-top molecules. In these molecules transitions with $\Delta K \neq 0$ are strongly forbidden, so that during a sufficiently strong cooling of a gas of these molecules, all the molecules are found in levels $J = |K|$ and the number of molecules in a given level $J = |K|$ is determined by the summation over all states $J'K$ with $J' > J$ at the initial temperature of the gas. Because of this distribution of molecules over the levels, there will be a state of negative temperature for transitions with $\Delta K \neq 0$.

4. We can estimate the efficiency of similar systems:

$$\eta = E_{\text{rad}}/E_{\text{abs}}. \tag{8}$$

The maximum value of the efficiency will be obtained if the establishment of equilibrium between the levels of the discrete part of the spectrum of one of the subsystems and the emission of stored energy occur so rapidly that the second subsystem does not change temperature significantly during this time:

$$\eta_{max} = \frac{1}{2}(n_i - n_k)\, h\nu_{ik} \Bigg/ \int_{T_i}^{T_f} \tilde{C}_v(T)\, dT, \tag{9}$$

where n_i is the population of the working level of the "heated" subsystem, and n_k is the population of the working level of the "cooled" subsystem, whereby $E_i > E_k$; $\tilde{C}_V$ is the specific heat of the "heated" subsystem; $\frac{1}{2}h\nu_{ik}(n_i - n_k)$ is the maximum radiated energy.

Sufficiently fast heating of the system plays an important role in this method for increasing negative temperatures.

In some cases this can be accomplished by using fast chemical reactions or shock waves.

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[1] A. Farkas, Parahydrogen, Orthohydrogen, and Heavy Hydrogen (Russ. Transl.), ONTI, 1936.

[2] C. H. Townes and A. L. Shawlow, Microwave Spectroscopy, McGraw, New York, 1955.

Translated by L. M. Matarrese
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