THIRD LAW OF THERMODYNAMICS AND QUANTUM-STATISTICAL SYSTEMS

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Some consequences of the third law of thermodynamics (TLT) in the Ising-like systems are studied and the cases when TLT is violated are found.

It is well known that the first and the second principle of thermodynamics can be deduced generally - independetly of the concrete properties of the considered physical systems. In that sense they are the general principles of thermodynamics. However, the third law of thermodynamics can not be deduced generally from the statistical mechanics.

TLT asserts: The entropy of the system at T = 0 does not depend on external parameters $\{q_i;\ i = 1,2,...\}$, i.e.

$$S(T = 0;\ \{q_i\}) = S(T = 0;\ \{\bar{q}_i\}) = S_0 = \text{const.} \tag{1}$$

At T = 0 quantum properties of the system are essential, since TLT is directly connected with them. The constant S_0 can be calculated in the framework of statistical mechanics and does not depend on the energy spectrum of the system, what essentially claims TLT.

All systems studied at the time when TLT was formulated, suggested the particular choise $S_0 = 0$, i.e.

$$S^* = \lim_{T\to 0} \lim_{N\to\infty} \frac{S}{N} = S_0 = 0 \tag{2}$$

It must be mentioned that it is reasonable to construct the statistical enetropy at T = 0 by the ground state degeneracy $g_0(N)$

$$\tilde{S} = K \lim_{N\to\infty} \frac{\ln g_0(N)}{N} \tag{3}$$

The comparison of S^* and $\tilde{S}$ will be given later.

As it is known the systems with the Bose-Einstein statistics (phonos and photons) and Fermi statistics (electrons in metals and quasiparticles in ^3He are examples where TLT is not violated because $S_0 = 0$. However, and that is subject of this paper, one can construct some model systems [1] in which, beside the contribution from the ground state degeneracy $g_0(N)$, excited states give dominant contribution to S^*. This contribution is essential in the case when the degeneracy of the excited states $(g_1, g_2, \ldots)$ is of the order a^N, when $a>1$.

Examples of the systems whose entropy depends on the energy spectrum of the system are Ising-like systems in 1-D, 2-D and 3-D, with the hamiltonian

$$H_N = \sum_{\vec{r}\vec{c}} g(S^z_{\vec{r}}, S^z_{\vec{r}+\vec{c}}) + \sum_{\vec{r}} f(S^z_{\vec{r}}) \tag{4}$$

$\sum_{\vec{r}}$ means summation over nearest neighbours. $g(S^z_{\vec{r}}, S^z_{\vec{r}+\vec{c}})$ and $f(S^z_{\vec{r}})$ are generalized exchange interaction, generalized magnetic field and generalized single ion anysitropy respectively.

One can shaw [2] that in the presence of appropriete symetry of the functions $g(S^z_{\vec{r}}, S^z_{\vec{r}+\vec{c}})$ and $f(S^z_{\vec{r}})$ it is possible to realize $S_0 \neq 0$. Let us mention, very shortly, two interesting examples studied in ref. [2]. We shall study only 1-D systems with nerest neighborus interaction. That means

$$g(S^z_{\vec{r}}, S^z_{\vec{r}+\vec{c}}) = g(S^z_i, S^z_{i+1}); \quad f(S^z_{\vec{r}}) = f(S^z_i)$$

a) $g_{11} = g_{-11} = g_{-1-1} = g; \quad f_o = o; \ g_{io} = o; \ i = 1, o, -1$

$S^* = K \cdot \ln 2; \ \tilde{S} = o, \ (g_o(N) = 1)$

b) $g_{oo} = g_{-1o} = o; \quad g_{ij} = g; \quad (i,j) \neq (o,o), (-1,o)$

$f_{-1} = f_1 = g_o; \quad f_o = o$

$S^* = \ln \frac{3+\sqrt{5}}{2}; \ \tilde{S} = K \cdot \ln(1+\sqrt{2})$

Inequality $S^* > S$ in a) and b) demonstrates that S^* does not reflect necessarily the ground state degeneracy, because the first excited states contribute to the entropy, as it was mentioned above.

Finaly we shall study in more details an example not described in [2], which illustrates the dependence of S^* (T=0) on external parameters, i.e. violates TLT.

Under consideration is the system of Jahn-Teller (JT) ions displaced in 1-d chain. In the Ref.[3] the hamiltonian of the system is written in the form

$$H_N = \sum_{i=1}^{n-1} \left[I_1 S_i^z S_{i+1}^z + I_2 \sigma_i^z \sigma_{i+1}^z + I_3 S_i^z S_{i+1}^z \sigma_i^z \sigma_{i+1}^z \right] - h \sum_{i=1}^{n} S_i^z \qquad (5)$$

σ_i is the pseudospin of j-th centre and it characterises the orbital levels of JT ions surrounding atoms, $\vec{S}_i$ is the spin of j-th centre ($S_i^z = 1/2$), I_1 and I_2 are exchange integrals between spins and pseudospins respectively, and I_3 describes the influence of JT orbitals on the exchange interaction.

In the case of the antiferromagnetic interaction between the spins ($I_1 > 0$) with the suitable choice of parameters I_1, I_2, I_3 and h

$$I_1 > 0; \quad I_2 > 0; \quad I_3 > 0$$

$$I_1 > I_2 > I_3 > 0; \quad h \approx h_c = 2\,(I_1 - I_2)$$

one can obtain that $S^* = K \ln \frac{1+\sqrt{5}}{2}$

In the case $h \neq h_c$ one gets $S^* = 0$.

This means that the entropy depends on the external parameters such as h, and on the structure of the energy levels of the system. It seems that using such a system is possible to attain the absolute zero temperature. Formally this conclusion is correct, but the hamiltonian (5) is rather unreal because it does not include the interaction of the system with other subsystems-like phonons. These interactions will destroy the big degeneracy of the ground and first excited state.

Then an achievement of the absolute-zero temperature is not possible.

REFERENCES

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