

Phys 7230

Midterm

March 17

Consider a spin 1/2 particle fixed in space in the presence of magnetic field H . The energy E of such a system can take one of the two values given by

$$E_s = -\mu H s,$$

where μ is the magnetic moment, and s takes values -1 and 1 .

(a) Calculate the partition function of this system.

Solution

$$Z = \sum_{s=1,-1} e^{-\frac{E_s}{T}} = e^{\frac{\mu H}{T}} + e^{-\frac{\mu H}{T}} = 2 \cosh\left(\frac{\mu H}{T}\right).$$

(b) Calculate the Helmholtz free energy F , entropy S , and heat capacity c . Calculate also energy E as a function of temperature T .

Solution

$$F = -T \log Z = -T \log \left[2 \cosh\left(\frac{\mu H}{T}\right) \right].$$

$$S = -\frac{\partial F}{\partial T} = \log \left[2 \cosh\left(\frac{\mu H}{T}\right) \right] - \frac{\mu H}{T} \tanh\left(\frac{\mu H}{T}\right).$$

$$c = T \frac{\partial S}{\partial T} = \left(\frac{\mu H}{T \cosh\left(\frac{\mu H}{T}\right)} \right)^2.$$

At small T the specific heat decays exponentially,

$$c \approx \left(\frac{2\mu H}{T} \right)^2 e^{-\frac{2\mu H}{T}}, \quad T \ll \mu H.$$

At large T the specific heat decays as a power law

$$c \approx \left(\frac{\mu H}{T} \right)^2, \quad T \gg \mu H.$$

Finally, energy E is given by

$$E = F + TS = -\mu H \tanh\left(\frac{\mu H}{T}\right).$$

If the temperature is taken to zero, the energy goes to $-\mu H$, that is, the spin is in its ground state. If the temperature is taken to infinity, the energy goes to zero. This is due to spin spending equal time in ground and excited states, which are exactly opposite to each other in value. So the average energy is then equal to zero.

Notice that the heat capacity can be alternatively calculated as

$$c = \frac{\partial E}{\partial T}.$$

(c) Average magnetization M is defined as in

$$M = \mu \sum_{s=-1,1} s p_s,$$

where p_s is the probability for the variable s to take values 1 and -1 . Show that once the free energy F is known, one can compute the average magnetization by using

$$M = \frac{\partial F}{\partial H}.$$

Use this relation to find the average magnetization M .

Magnetic susceptibility χ is defined in the following way

$$\chi = \left. \frac{\partial M}{\partial H} \right|_{H=0}.$$

Calculate magnetic susceptibility for this problem. What happens to the magnetic susceptibility as temperature is taken to 0?

Solution

p_s is the probability that the energy of the spin is E_s . In the Gibbs distribution, it takes values

$$p_s = \frac{e^{-\frac{E_s}{T}}}{Z}.$$

Then the average magnetization is given by

$$M = \mu \sum_{s=-1,1} \frac{s e^{\frac{\mu H s}{T}}}{Z}$$

On the other hand,

$$F = -T \log Z = -T \log \left(\sum_{s=-1,1} e^{\frac{\mu H s}{T}} \right).$$

Differentiating this expression with respect to H we find

$$-\frac{\partial F}{\partial H} = \frac{\mu}{Z} \sum_{s=1,-1} s e^{\frac{\mu H}{T}},$$

which coincides with the definition of M . Now we calculate M .

$$M = -\frac{\partial F}{\partial H} = \mu \tanh\left(\frac{\mu H}{T}\right).$$

Finally, we calculate the magnetic susceptibility

$$\chi = \left. \frac{\partial M}{\partial H} \right|_{H=0} = \frac{\mu^2}{T}.$$

Magnetic susceptibility diverges as $1/T$ as temperature is taken to zero.

(d) Calculate F , S , c , and χ for the system which consists of N spins.

Solution

F is an extensive quantity, thus

$$F_N = NF,$$

where F_N is the free energy of N spins, and F is the free energy of one spin calculated above. Since S , c , and χ are all derived by differentiating F , S_N , c_N , and χ_N will all be N times the appropriate quantities for one spin.

More detailed calculate takes into account that the energy of the system consists of sums of energies of each spin, and each of them is summed over independently in the partition function. So the partition function for N spins is $Z_N = Z^N$, where Z is the partition function for one spin. Thus, $F_N = NF$, and so on.

(e) Suppose this spin system is put into a state where its temperature is negative $T < 0$ (this is, in fact, possible and has been achieved experimentally with nuclear spins). Then it is brought into a contact with a large heat reservoir which is at room temperature $T_{\text{reservoir}} \sim +300K$. Will the energy of the spin system be increasing or decreasing, and how will the temperature of the spin system be changing in time, until it reaches equilibrium with the reservoir? Use the law of entropy increase and apply it to the combined spin+reservoir system to answer this question.

Solution

Negative temperatures are possible in the systems whose spectrum is bounded from above. If the temperature is negative and large, $T < 0$ and $|T| \gg \mu H$, the results of the end of section (b) where energy is calculated imply that the energy becomes $E = \mu H$. In other words, at large negative temperature the system spends most of its time in its

excited state. This can be contrasted with the situation at infinite temperature where the system divides its time equally between all states, and the zero temperature situation where the system is in its ground state.

This in fact means that the negative temperatures should be thought of as not being below positive temperatures, but rather being *above infinite temperature*. As the temperature of the system is increased, its energy increases too, and reaches certain value as the temperature becomes infinite. To increase its energy further, one needs to make the temperature negative infinite, and then continue to increase it until it hits zero from below, which is, in effect, a maximum possible temperature.

This could be expressed mathematically by introducing a notation $\beta = -\frac{1}{T}$. This parameter changes from $-\infty$ to 0, as temperature is taken from 0 to ∞ . As temperature is taken from $-\infty$ to 0, β changes from 0 to ∞ . Then the energy of the spin can be written as

$$E = \mu H \tanh(\beta\mu H),$$

which is a monotonously increasing function of β .

Already these considerations lead to the conclusion that a system at negative temperature is *hotter* than a system at positive temperature. Thus if it is brought in contact with a reservoir at positive temperature, its temperature will *decrease*, go through $-\infty$, then ∞ , and then continue to decrease further until it reaches the temperature of the reservoir.

The same conclusion can be reached via analysis of the entropy. The total entropy of the combined system is given by

$$S(E) = S(E) + S_{\text{reservoir}}(E_{\text{tot}} - E).$$

$$\frac{\partial S}{\partial E} = \frac{\partial S}{\partial E} - \frac{\partial S_{\text{reservoir}}(E_{\text{tot}} - E)}{\partial E_{\text{tot}}} = \frac{1}{T} - \frac{1}{T_{\text{reservoir}}} < 0$$

since $T < 0$, $T_{\text{reservoir}} > 0$. Thus if E increases, total entropy will decrease. Since the total entropy should always increase (law of entropy increase), the energy E will be decreasing. In other words, the energy will flow from the system at negative temperature towards the reservoir at positive temperature.

Useful formulae

Canonical ensemble.

- Partition function $Z = \sum_n e^{-\frac{E_n}{T}}$, where E_n are the energy levels of the system.
- Free energy $F = -T \log Z$. Energy of the system $E = F + TS$. $dF = -SdT - PdV + \mu dN$, $dE = TdS - PdV + \mu dN$.
- Probability that the system's energy is equal to E_n is $p_n = \frac{1}{Z} e^{-\frac{E_n}{T}}$.

Grand canonical ensemble.

- Partition function $Z = \sum_n e^{-\frac{E_n}{T} + \frac{\mu N_n}{T}}$, where E_n are the energy levels of the system, and N_n is the number of particles at this level.
- Grand canonical free energy $\Omega = -T \log Z$. $d\Omega = -TdS - PdV - Nd\mu$. $\Omega = F - \mu N$.
- Probability that the system's energy is equal to E_n if it has N_n particles is $p_n = \frac{1}{Z} e^{-\frac{E_n}{T} + \frac{\mu N_n}{T}}$.

Other formulae

- Heat capacity is the amount of heat pumped into the system to increase its temperature by dT . At fixed volume it is given by $c_v = T \left(\frac{\partial S}{\partial T} \right)_V$. At fixed pressure it is given by $c_p = T \left(\frac{\partial S}{\partial T} \right)_P$. Specific heat is the heat capacity per particle.
- Maxwell relations are relations between derivatives which follow from the fact that partial second derivatives of thermodynamic potentials do not depend on the order of differentiation. For example,

$$dE = TdS - PdV \rightarrow \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V.$$

- Quasiclassical approximation to the partition function of a particle

$$Z = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} e^{-\frac{p^2}{2mT}}$$

- Equipartition theorem: specific heat of a quasiclassical system is equal to 1/2 per degree of freedom which enters its energy quadratically.
- Fermi-Dirac and Bose-Einstein grand canonical free energy $\Omega = -Ts \sum_n \ln \left(1 + s e^{-\frac{E_n}{T} + \frac{\mu}{T}} \right)$, where $s = 1$ for Fermi-Dirac and $s = -1$ for Bose-Einstein distributions.
- Bose-Einstein distribution $N = N_0 + \int \frac{d^3p d^3x}{(2\pi\hbar)^3} \frac{1}{e^{\frac{p^2}{2mT} - \frac{\mu}{T}} - 1}$, where N is the total number of particles, and N_0 are the particles in the condensate. $N_0 = 0$ at $T > T_c$, while $\mu = 0$ at $T < T_c$.