

Lecture

From statistical physics to thermodynamics

We saw from the paramagnetic example that the average energy of the N -dipole system is

$$U \equiv \langle E \rangle = - N \mu B \tanh\left(\frac{\mu B}{kT}\right)$$

by definition

the number of dipoles

magnetic field

dipole's magnetic moment

Temperature

Thus the average energy U is a function of the total number of dipoles N , the magnetic field B and the temperature T .

$$U(T, N, B)$$

We include only T, N and B in the list (and NOT μ) because μ is a

macroscopic experiment we can change T, N or B , but not μ .

The relation

$$U(T, N, B) = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

is called an EQUATION OF STATE in THERMODYNAMICS. There is a danger of confusion between a THERMODYNAMIC STATE and a STATISTICAL PHYSICS STATE.

(1) A thermodynamic state, for this case, is given by T, N, B

(2) A statistical physics state is

$$(j_1, j_2, \dots, j_N)$$

with each $j_k = \pm \mu$.

When we compute the canonical probability

$$P_j = \frac{e^{-\beta E_j}}{\sum}$$

we consider the thermodynamic state fixed. Namely the temperature T 's fixed and also N and B .

We know from practice that the thermodynamic state (T, N, B) can be changed and it is useful to change it.

Question: How can we relate the change in the THERMODYNAMIC STATE with the change of the probability to be in a STATISTICAL PHYSICS STATE?

Start from the definition of the average energy

$$U = \sum_j E_j P_j$$

It is good to remember the paramagnetic case, as an example. Then

$$U(T, N, B)$$

Now E_j depends on B and NOT on β

$$E_j(B)$$

On the other hand, the probability P_j depends on β and on B THROUGH E_j

$$P_j(\beta, E_j(B))$$

In general, a variation of the average energy U , when T or B varies is given by

$$dU = \underbrace{\sum_j E_j \cdot dP_j}_{\textcircled{1}} + \underbrace{\sum_j P_j \cdot dE_j}_{\textcircled{2}}$$

Our goal is to understand the macroscopic meaning of the terms $\textcircled{1}$ and $\textcircled{2}$.

We consider first term number $\textcircled{1}$. This term depends only on the variation of the probabilities P_j . We can express it only in terms of P_j as follows:

From

$$P_j = \frac{e^{-\beta E_j}}{\Omega}$$

we get

$$E_j = -\frac{1}{\beta} (\ln \Omega + \ln P_j)$$

so

$$\sum_j E_j \cdot dP_j = -\frac{1}{\beta} \sum_j (\ln \Omega + \ln P_j) dP_j =$$

$$= -\frac{1}{\beta} \ln 2 \sum_j dP_j - \frac{1}{\beta} \sum_j dP_j (\ln P_j)$$

Now, from

$$\sum_j P_j = 1$$

we get

$$\sum_j dP_j = 0$$

So

$$\sum_j E_j dP_j = -\frac{1}{\beta} \sum_j dP_j (\ln P_j) =$$

$$= -\frac{1}{\beta} d\left(\sum_j P_j \ln P_j\right)$$

using again

$$\sum_j dP_j = 0$$

Remember that

$$S = -k_B \sum_j P_j \ln P_j$$

we get then

$$\sum_j E_j dP_j = T dS$$

The variation δU due only to the probability distribution variation is equal with the temperature times the entropy variation.

The second term

$$\sum_j P_j dE_j$$

can be written as

$$\sum_j P_j \frac{dE_j}{dB} dB$$

because E_j will change with B .

But

$$E_j = -\mu_B (j_1 + j_2 + \dots + j_N) B$$

$$\text{So } \sum_j P_j \frac{dE_j}{dB} dB = - \sum_j P_j (j_1 + \dots + j_N) dB =$$

$$= - M dB$$

when M is the average total magnetic moment.

So

$$\sum_j P_j dE_j = - M dB$$

So the second part of change in the average energy is attributed to the change in the external magnetic field B .

Conclusion

$$dU = Tds - MdB$$

The interpretation of this result is

$$dU = \text{HEAT TRANSFERED} + \text{WORK TRANSFERED}$$

$$\text{HEAT TRANSFERED} = Tds$$

$$\text{WORK TRANSFERED} = -MdB$$

This is the FIRST LAW OF THERMODYNAMICS. !

Remember that dU referred to the variation of the mean energy as the THERMODYNAMIC STATE varied

$$\downarrow (T, N, B)$$

$$\text{So } dU = \left(\frac{\partial U}{\partial T} \right)_{N, B} dT + \left(\frac{\partial U}{\partial B} \right)_{T, N} dB$$

and $U(T, N, B)$ is a function of the thermodynamic state.

Because the thermodynamic state is (T, N, B) we must have

$$S(T, N, B)$$

and $M(T, N, B)$.

Indeed, we computed

$$M(T, N, B) = N\mu \tanh\left(\frac{\mu B}{kT}\right)$$

The entropy can be computed also

$$\begin{aligned} S^d &= -k \sum_j P_j \ln P_j = -k \sum_j \frac{e^{-\beta E_j}}{Z} \ln\left(\frac{e^{-\beta E_j}}{Z}\right) \\ &= -k \frac{1}{Z} \sum_j e^{-\beta E_j} [-\beta E_j - \ln Z] = \\ &= -k (-\beta) \sum_j E_j \frac{e^{-\beta E_j}}{Z} + k \frac{\ln Z}{Z} \sum_j e^{-\beta E_j} = \\ &= k\beta \langle E \rangle + k \ln Z \end{aligned}$$

So

$$S^d = \frac{k}{kT} U + k \ln Z$$

or

$$S^d = \frac{1}{T} U + k \ln Z$$

(*)

We computed

$$U(T, N, B) = -N\mu B \tanh(\mu\beta B)$$

So

$$S(T, N, B) = -\frac{N\mu B}{T} \tanh\left(\frac{\mu B}{kT}\right) + k \ln \Omega$$

$$S(T, N, B) = -\frac{N\mu B}{T} \tanh\left(\frac{\mu B}{kT}\right) + k \ln \left(2^N \left[\cosh\left(\frac{\mu B}{kT}\right) \right]^N \right)$$

This formula is presented just to show that indeed the entropy depends on the thermodynamic state (T, N, B)

Notice that the relation (*) show us that

$$-kT \ln \Omega = U - TS \quad (**)$$

We will come back later and discuss this relation between the partition function Ω , the average energy and the entropy of the system.