

Magnetic Systems and Statistical Physics — 18.03, 2019

*Prof. dr hab. Antoni Mitus**Scribe: Krzysztof Agieńczyk*

1 Overview

In the last lecture we talked about internal and free energy, thermodynamics potentials and entropy..

In this lecture we expanded on thermodynamics potentials, functions of state in magnetism and statistical physics.

2 Reminder

If you need an introductory book for this course, try Reif's[1].

There are a few important equations from the last lecture. Let's recall them.

Change of internal energy:

$$dU = TdS - pdV \quad (1)$$

Free energy:

$$F = U - TS \quad (2)$$

Gibbs free energy

$$G = U - TS + pV \quad (3)$$

and Internal Energy

$$U = -T^2 \left(\frac{\partial F}{\partial T} \right) V \quad (4)$$

In the previous lecture we discussed some important thermodynamics potentials like heat capacity, which is

$$C_x = \left(\frac{\Delta Q}{\Delta T} \right)_x \quad (5)$$

where x is some parameter like p, V, etc. meaning we measure heat capacity with constant x (parameter).

Ready to use formulas for heat capacity are below. The explanation of them is left as an exercise.

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (6)$$

$$C_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial U}{\partial T} \right)_p \quad (7)$$

Given free energy we can calculate internal energy and heat capacity.

2.1 Expansion coefficient

The expansion coefficient tells us how the system reacts to expansion. We denote it by β .

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (8)$$

2.2 Isothermal compressibility

The isothermal compressibility tells us how the system reacts to the change of external pressure. We denote it by κ

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (9)$$

Example 1 Let us assume ideal gas ($pV = RT$) and we want to calculate β .

$$V = \frac{RT}{p} \implies \left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p} \implies \beta = \frac{1}{V} \frac{R}{p} = \frac{R}{RT} = \frac{1}{T} \quad (10)$$

Example 2 Let us do the same for κ ¹

$$V = \frac{RT}{p} \implies \left(\frac{\partial V}{\partial p} \right)_T = -\frac{RT}{p^2} \implies \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{p} \implies \kappa_T = \frac{1}{p} \quad (11)$$

2.3 Magnetic Systems

In the magnetic field, change of internal energy can be calculated like this:

$$dU = TdS - MdH \quad (12)$$

where M is magnetisation and H is external magnetic field. Using this and previous equations we can substitute $dF = d(U - TS) = dU - dTS = TdS - MdH - dTS - TdS$. This means

$$M = -\left(\frac{\partial F}{\partial H} \right)_T \quad (13)$$

3 Functions of state in thermodynamics

What is really the problem? Well, work in thermodynamics is denoted as

$$\delta W = pdV \quad (14)$$

This means that if we first change the volume and pressure later, the work will be different than if we first increased pressure and then changed volume. This means work is dependant on path, not only states.

¹This was left as an exercise by prof and done by me, I cannot be sure if it's correct - kagienicz

3.1 Analogy with mechanics

Let's have a force $\vec{F}(\vec{r})$. If work is independent of the trajectory, then F is potential. Rotation/curl of F is calculated as

$$\text{rot}\vec{F} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ F_x & F_y & F_z \end{vmatrix} \quad (15)$$

If this rotation is equal to 0, then the force is potential.

For two variables

$$\delta F(x, y) = X(x, y)dx + Y(x, y)dy \quad (16)$$

where the right hand side can be expressed as a scalar product of two vectors.

$$\delta F(x, y) = [X, Y, 0] \cdot [dx, dy, dz] = \vec{f} * d\vec{r} \quad (17)$$

For \vec{f} to be a function of state $\text{rot}\vec{f}$ has to be equal to 0. This is satisfied if and only if $\frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x}$. This is called cross relation.

3.2 Maxwell relation

From experiment we know internal energy is a function of state. This means cross relation holds.

$$dU = TdS - pdV = T(S, V) * dS - p(S, V)dV \quad (18)$$

$$\left(\frac{\partial T}{\partial V}\right) = -\left(\frac{\partial p}{\partial S}\right)_V \quad (19)$$

4 Statistical Physics

4.1 System

All of the systems (of atoms, system of single magnetic momentum, etc.) allow energy states e_1, e_2, \dots . These states can be either discrete or continuous. System can exchange energy or particles with the environment. We will assume this environment has constant temperature T. In equilibrium, system also has temperature T, equal to the temperature of the environment. Energy of small system is not constant but fluctuates.

Question What is the probability P_r that the small system is in state r with energy e_r ?

4.2 Canonical distribution (Gibbs-Boltzman)

Definition 1. Take N copies of the system and let us isolate our states from the outside. They can however exchange energy and particles between themselves. In such case, the total energy E is constant.

References

- [1] Reif F. Fundamentals of Statistical and Thermal Physics *Waveland Press, Inc.*, 2013.