Statistische Mechanik von Gittersystemen / Statistical mechanics of lattice systems

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1 Overview

Basic goal of statistical mechanics is to give a <u>mechanical model</u> of <u>thermodynamic behaviour.</u>

We have to undestand what thermodynamics is about and what could be a mechical model of it.

The appropriate mechanical model will be a probabilistic model of the motion of atoms (or in general of very simple microscopic constituents of matter, e.g. in magnetic phenomena one is concerned mostly with the local magnetization in a solid)

Our book focus on very simple discrete probabilistic models (real mechanical models are continuous, i.e. their state is described by continuous variables not discrete, or in the quantum case the state of the system is even described by a vector in infinite dimensional Hilbert space). These models are unrealistic but somehow capture the basic phenomena which one would like to describe.

My point today is to have a vague idea on which these phenomena.

2 Thermodynamics

Thermodynamics is the physical theory which describe the macroscopic states and transformations of matter composed by many individual atoms (or simple components).

A basic example of a thermodynamical system is a gas. From the point of view of mechanics (or atomic physics) a gas is just a collection of atoms which move freely in a given portion of space. In first approx. one think about the different atoms to be "independent" one another. The atoms do not "see each other" and they move as billiard balls on the table, reflecting on the walls of the container.

$N \approx 10^{23}$ typical number of atoms involved in the macroscopic description. Each atom has a position and a velocity, i.e. it is described by a point in $\mathbb{R}^6 \Rightarrow$ The state of this system is a point in $\mathbb{R}^{6N}$. We do not have a good intuition of the geometry of such very large Euclidean spaces.

In particular the macroscopic state of the gas does not really depend on the precise value of all these coordinates. At our scale we can only perceive/control few characteristics of this gas:

- N the number of particles,

- V volume they occupy,

- U their total energy (i.e. the capacity to produce work, this is somehow a derived quantity, it corresponds to the sum of the kinetic energy of each particle and their potential energy).

In particular situations there could be also other quantities:

- P total momentum. In this case the total energy is $E = N\,(P^2/2m) + U$

- M total magnetic momentum. In case of magnetic materials.

- $\tilde{M}$ total rotational momentum: a star.

What make these quantities relevant is that in absence of interactions with external world they are constants of motion in the mechanical system.

$$Z \in \mathbb{R}^{6N} \to (U, V, N)$$

It is an empirical fact that (U, V, N) describe completely the macroscopic system at **equilibrium**: you prepare the system and allow it to settle in a state where you do not see any more macroscopic change. The variables (U, V, N) only make sense at equilibrium. If the system is not in equilibrium they do not **exists**. They parametrize only the manifold of equilibrium states of the system.
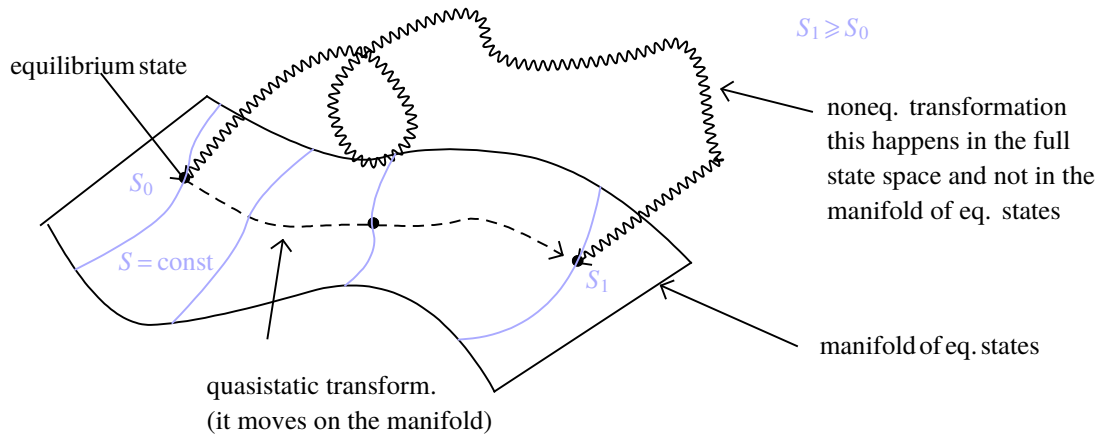
One can also look separately at different parts $i = 1, \ldots, K$ of this big systems as subsystems and associate to them $(U_i, V_i, N_i)_{i=1,\ldots,K}$ and one has the relation

$$U = U_1 + \cdots + U_K, \quad V = V_1 + \cdots + V_K, \quad N = N_1 + \cdots + N_K,$$

i.e. these quantities are <u>extensive</u>: they are additive on subsystems.

One typical situation is when we have two systems (U_1, V_1, N_1) and (U_2, V_2, N_2) (imagine two boxes with gas inside) and we put them together, (i.e. we remove a wall between the two boxes, or we allow the wall to move – a piston, or we allow the particles to exchange energy via the wall). When you allow interaction only some functions of (U_1, V_1, N_1) and (U_2, V_2, N_2) remain constant, for example if you allow exchange of energy one still has that $U_1 + U_2$ remain constant in time. If we don't allow immigration/emigration of particles then we must have $N_1 + N_2$ constant and if we don't allow change of total volume we must have $V_1 + V_2$.

So this global system could evolve until it settle in a new equilibrium state (see picture above) described again by new variables $(U_1, V_1, N_1, U_2, V_2, N_2)$. Which is this new state???

The basic postulate of thermodynamics (in these lectures) is that for every system there exists a function $S(U_i, V_i, N_i)$ the entropy which depends only on the kind of system and such that the entropy of the sum of two subsystems in equilibrium is given by the sum the entropies (i.e. the entropy is extensive) and moreover the entropy <u>always increase</u> in time for a closed system, i.e. before and after a transformation between equilibrium states. This tells me that if $(U_1, V_1, N_1, U_2, V_2, N_2)$ is an equilibrium state of the coupled system then

$$S(U_1, V_1, N_1, U_2, V_2, N_2) = S(U_1, V_1, N_1) + S(U_2, V_2, N_2)$$

$$\geqslant S(U_1', V_1', N_1') + S(U_2', V_2', N_2')$$

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where $(U_1', V_1', N_1', U_2', V_2', N_2')$ is any other state describing the two subsystems which can evolve into $(U_1, V_1, N_1, U_2, V_2, N_2)$. In particular $S(U_1, V_1, N_1, U_2, V_2, N_2)$ maximises $S(U_1', V_1', N_1') + S(U_2', V_2', N_2')$ among all states of the subsystems which can lead to the final state.

This is the basic variational principle on which thermodynamics is based.

Let's see this principle at work: imagine we allow only exchange of energy (in the form of heat) but not of volume or matter, then letting $U = U_1 + U_2$ we need to have

$$S(U_1, V_1, N_1, U_2, V_2, N_2) = \max_{x \in [0,U]} [S(U - x, V_1, N_1) + S(x, V_2, N_2)]$$

and moreover $U_1 = U - x_*$, $U_2 = x_*$ where x_* is the maximum point. Then we must have

$$0 = \frac{\partial}{\partial x} S(U - x, V_1, N_1) + \frac{\partial}{\partial x} S(x, V_2, N_2)$$

$$= -\left(\frac{\partial S}{\partial U}\right)_{V,N} (U - x, V_1, N_1) + \left(\frac{\partial S}{\partial U}\right)_{V,N} (x, V_2, N_2)$$

that is

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} (U_2, V_2, N_2) = \left(\frac{\partial S}{\partial U}\right)_{V,N} (U_1, V_1, N_1)$$

calling $\beta = \left(\frac{\partial S}{\partial U}\right)_{V,N}$ one has $\beta(U_2, V_2, N_2) = \beta(U_1, V_1, N_1)$ in equilibrium, i.e. this β function has to be equal in the two subsystems in equilibrium. One call it the inverse temperature, i.e. $T = 1/\beta$ is the absolute temperature, measures in Kelvin.

From the same argument one derives also that energy flows from system at higher temperature to systems at lower temperatures.

For usual materials one has $\beta > 0$ (not always the case however, there exists systems at negative temperature), i.e. entropy increases with the energy.

In real life a common situation is when we have a "small system" in thermal contact with a "big system", e.g. think about an object in a room, then the two have the same temperature in equilibrium. If the second system is very big then the change in internal energy given by exchanges with the first system is negligible, so in the computation above, if we denote by y the energy of the small system we have (by Taylor expansion)

$$S(y, V_1, N_1) + S(U - y, V_2, N_2) \approx S(y, V_1, N_1) + S(U, V_2, N_2) - y \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N} (U, V_2, N_2)}_{\beta(U, V_2, N_2) = \beta(y, V_1, N_1)}$$

$$\approx S(y, V_1, N_1) - \beta y + \text{const} + \cdots$$

So in thermal contact with "reservoir" at temperature $\beta = \beta(U, V_2, N_2)$ the first system will try to maximise the function

$$y \mapsto S(y, V_1, N_1) - \beta y$$

to be in equilibrium. The function

$$F(\beta, V_1, N_1) = \max_{U_1} [S(U_1, V_1, N_1) - \beta U_1]$$

is called "free energy": it describes the work available to a system which is in thermal equilibrium with a reservoir at temperature β.

We say that β is the conjugate variable to the energy, i.e. by controlling β I can control the quantity of internal energy. (This relation is related with Legendre transformation in the theory of convex functions).

You see here that various situations give rise to various variational principles involving the entropy and the other thermodynamic quantities.

3 Statistical mechanics

Stat mech wants to derive a connection between the description involving all the $6N \approx 10^{23}$ degrees of freedom of a general mechanical motion of the system and the few degrees of freedom in thermodynamic equilibrium. This connection goes via Boltzmann "discovery":

$$S(U,V,N) \propto \log \Omega(U,V,N)$$

where $\Omega(U,V,N)$ is the number of microscopic configurations (measured in an appropriate way) compatible with the given macroscopic ones (U,V,N). One can say this probabilistically by saying that the probability P to observe a given macroscopic state (U,V,N) is given by

$$P \propto \Omega(U,V,N) \propto e^{S(U,V,N)/k}.$$

Underlying this last equivalence is the idea that all the microscopic states X are equiprobable

$$P(X) \propto 1$$

This formula gives a connection with probability theory.

When the system is in thermodynamic equilibrium with a larger system at temperature β then the probability to observe a given configuration X is given by

$$P(X) \propto e^{-\beta U(X)}$$

then

$$\sum_X e^{-\beta U(X)} = \sum_U \Omega(U,V,N) e^{-\beta U} = \sum_U e^{-\beta U + S(U)/k} \approx e^{\max_U (S(U) - k\beta U)/k} \approx e^{F(\beta,V,N)}$$

in particular we have found the relation

$$F(\beta,V,N) = \log \sum_X e^{-\beta U(X)}$$

which will be important in the rest of the book.

In the passage from the statistical mechanical model to the thermodynamic quantities one important step is the infinite volume (or infinite # of particles) limit, i.e. we really want to compute for $V = vN$

$$F(\beta,v,1) = \frac{1}{N}F(\beta,vN,N) = \lim_{N \to \infty} \frac{1}{N}F(\beta,vN,N) = \lim_{N \to \infty} \frac{1}{N}\log \sum_X e^{-\beta U(X)}.$$

We want to show:

- that this limit exists (so that all the quantities we compute are extensive)

- we want to see appearing the variational principles.