

## Statistical Thermodynamics (review)

*In this course we will not provide a comprehensive introduction to elementary thermodynamics and statistical mechanics, which have already been covered in PHY 5524. It is, nevertheless, useful to briefly review the basic ideas and results from these subjects, which will serve as the starting point for the more advanced topics we will study in detail.*

### PHENOMENOLOGICAL THERMODYNAMICS

Thermodynamics has historically emerged much before its microscopic basis has been established. It describes the basic laws of thermal behavior, as directly observed in experiment. Remember, the early steam engines were built much before Boltzmann's discoveries...



In many novel materials we still do not have a well understood microscopic theory, but thermodynamic laws certainly apply, and they are useful in describing and interpreting the experimental data. We will, therefore, pause to refresh our memory of elementary

thermodynamics. A more detailed discussion can be found, for example, in the short but beautiful text by Enrico Fermi. We concentrate (as Fermi does) on a given example of a PVT system (liquid or gas). The results are then easily generalized, for example, to magnetic or other systems as well.

### The First Law

In equilibrium thermodynamics, one considers so-called "reversible" processes, where the physical state of the system is changed very slowly, in tiny, infinitesimal steps. The First Law is simply a statement of **energy conservation**. It states that the (infinitesimal) change of the internal energy  $E$  of the system is the sum of the work  $W$  done **against** an external force and the heat flow  $Q$  into the system

$$dE = dQ - dW.$$

For example, when a gas is expanding,  $dW = pdV$ , where  $p$  is the pressure of the gas, and  $dV$  is the volume change of the container.

#### *Heat capacity at constant volume*

if the gas is kept at the same volume, but is heated, then  $dE = dQ$ , and the (constant volume) heat capacity is defined as

$$C_V = \left( \frac{dQ}{dT} \right)_V = \left( \frac{\partial E}{\partial T} \right)_V.$$

#### *Heat capacity at constant pressure*

If we fix the pressure (then  $V$  is a function of  $V$  and  $T$ ), it is easy to show (**Problem 1**) that

$$C_V = \left( \frac{dQ}{dT} \right)_p = \left( \frac{\partial E}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p.$$

#### *Magnetic systems*

In magnetic systems, one usually considers the internal energy as an explicit function of the external magnetic field  $h$ . If the external field is infinitesimally varied, then the work

done is

$$dW = -Mdh,$$

where  $M$  is the magnetization of the sample. We can write

$$dU = dQ + Mdh.$$

### The Second Law

The "problem" with the first law by itself is that it does not tell us how much heat flows in or out of the system. It is only useful if we have a thermally isolated system ( $dQ = 0$ ), or if we already know the equation of state (i.e. the form of  $V(T, p)$ ).

The essential content of the Second law is that systems left alone tend to assume a most probable state, i.e. the one where as a function of time it explores as many configurations as allowed by energy conservation. It can be formulated in many ways, which can be shown to be mathematically equivalent (see book by Fermi). For example, the formulation by Clausius says:

*"Heat cannot spontaneously flow from a colder to a hotter body"*

But its most important consequence is that it introduces the concept of **entropy**. For any reversible process, the change of entropy is given by

$$dS = \frac{dQ}{T}.$$

If the system is thermally isolated ( $dQ = 0$ ), then any process **reversible** taking the system from state A to state B results in no change of entropy. However, based on the Second Law, one can show that if an isolated **irreversible** process is considered, then strictly

$$S(B) \geq S(A).$$

In other words, systems left to themselves tend to equilibrate by strictly **increasing their entropy**.

The First Law (for a gas) can now be written as

$$dE = TdS - pdV.$$

From this expression, we can write

$$T = \left( \frac{\partial E}{\partial S} \right)_V ; p = - \left( \frac{\partial E}{\partial V} \right)_S .$$

### The Third Law (Nernst Theorem)

For classical systems, the entropy is defined up to a reference constant, as it is not clear how degenerate is the ground state. In quantum mechanics, though, quantum tunneling tends to lift the ground state degeneracy, and in most systems the ground state is **not degenerate**. Therefore, the entropy of this state vanishes, i.e.

$$S(T = 0) = 0.$$

This result allows one to explicitly determine the precise numerical value of the entropy at any temperature directly from experimental data, as follows. We can express the entropy change in terms of the specific heat, and write

$$S(T) = \int_0^T \frac{C(T)}{T} dT.$$

Note that this expression immediately shows that  $C(T)$  has to vanish at  $T = 0$ , otherwise the integral would diverge. This expression is often used in interpreting experiments, for example on spin systems. Since the entropy reaches its maximal value for noninteracting spins, by looking at the temperature where  $S(T)$  starts to saturate, we can estimate the energy scale of the spin-spin interactions.

### The Free Energy

The internal energy must be regarded as an explicit function of the volume  $V$  and the entropy  $S$  as independent variables. However, this form is not particularly convenient to use, since we cannot directly control the entropy in an experiment. It is often more convenient to consider temperature  $T$  and the volume  $V$  as independent variables. To obtain an expression similar to the First Law, except with  $T$  and  $V$  as independent variables, we define the quantity

$$F = E - TS,$$

called the **free energy**. Mathematically, the free energy can be regarded as a "Legendre transform" of the internal energy, and its total differential can be computed using the chain

rule, as follows

$$\begin{aligned} dF &= dE - TdS - SdT \\ &= TdS - pdV - TdS - SdT, \end{aligned}$$

or

$$dF = -SdT - pdV.$$

**Important result:** "If the free energy is known as a function of its natural variables  $T$  and  $V$ , then from it all other thermodynamic quantities can be computed".

For example

$$S = - \left( \frac{\partial F}{\partial T} \right)_V ; p = - \left( \frac{\partial F}{\partial V} \right)_T.$$

We can also get the internal energy

$$E = F + T \left( \frac{\partial F}{\partial T} \right)_V,$$

and the specific heat

$$C_V = \left( \frac{dQ}{dT} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V.$$

For **magnetic systems**

$$dF = -SdT + Mdh,$$

and we get the magnetization

$$M = \left( \frac{\partial F}{\partial h} \right)_T,$$

and the magnetic susceptibility

$$\chi = \left( \frac{\partial M}{\partial h} \right)_T = \left( \frac{\partial^2 F}{\partial h^2} \right)_T.$$

### Stability conditions

Consider a gas at temperature  $T_o$  and volume  $V$ . Now let us assume that the volume of the system is suddenly increased and the system allowed to relax. The gas will rapidly expand, but this will correspond to an irreversible process. Assuming that the gas continues to be in contact with a heat reservoir at temperature  $T_o$ , some heat  $\Delta Q > 0$  must flow into the system. This is true, since without thermal contact the gas would simply cool down by

adiabatically expanding. If the heat contact is there, then the gas will re-heat by absorbing some heat from the reservoir. Note that this is consistent with the Second Law, which demands that the entropy strictly increases in such an irreversible process.

But what happens to the free energy? Well, according to the first law, the change of internal energy  $\Delta U = \Delta Q - \Delta W$ , but since the volume expanded rapidly, no work was actually done by the gas and thus  $\Delta U = \Delta Q$ . Now we note that even for an irreversible process, the change of entropy is

$$\Delta S \geq \int \frac{dQ}{T} = \frac{1}{T_o} \int dQ = \frac{\Delta Q}{T_o}.$$

We conclude that

$$\Delta Q \leq T_o \Delta S$$

for such an irreversible process. As a result, the change of the free energy

$$\Delta F = \Delta E - T_o \Delta S \leq 0.$$

We conclude that if the system is mechanically isolated, so no mechanical work is done in a given irreversible process, then the free energy of the system cannot increase. This argument is very general, and can be easily repeated for any thermodynamic system. Therefore:

*The free energy is at a minimum in the state of stable equilibrium.*

This result is very important, since we often resort to minimizing of the free energy with respect to some order parameter, in order to identify the thermodynamically stable states of the system.

These stability conditions, stating that at the equilibrium point the entropy is at a maximum and the free energy at a minimum, lead to few other important results. It is possible to show (see **Problem 2**) that it leads to the following conditions for the specific heat  $C_V$ , the isothermal compressibility  $\kappa_T$ , and the isoentropic compressibility  $\kappa_S$ , valid in the equilibrium state

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V \geq 0; \quad \kappa_T = - \left( \frac{\partial V}{\partial P} \right)_T \geq 0; \quad \kappa_S = - \left( \frac{\partial V}{\partial P} \right)_S \geq 0.$$

All these results are valid for systems with fixed numbers of particles  $N$ . Of course, these expressions are easy to generalized when instead, the chemical potential

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V}$$

is considered fixed (e.g. if we have a particle reservoir). In this case, we perform a Legendre transform with respect to  $N$ , defining the so-called "Grand Potential"

$$\Omega = F - \mu N,$$

so that, for example,

$$N = \left( \frac{\partial \Omega}{\partial \mu} \right)_T,$$

### MICROSCOPIC APPROACH

Statistical mechanics, as developed by Boltzmann, Gibbs, and others has provided the microscopic basis for thermodynamics. In this brief review, we will not repeat the discussions relating to the definitions of the various ensembles, or the derivations for the expression for the partition function. The central result that we will use over and over is the expression for the free energy in terms of the partition function

$$-\beta F = \ln Z,$$

where  $\beta = T^{-1}$ . Here and in the following we will use units of energy where the Boltzmann constant  $k_B = 1$ . The partition function generally takes the form

$$Z = \sum_n \exp\{-\beta E_n\},$$

where  $E_n$  are the energy states of the system. Our main task is to develop strategies how the partition function can be calculated.

We end this brief summary of Statistical Thermodynamics with a few comments about the microscopic definition of the entropy, following the discussion from Kadanoff (Chap. 8). For a closed system (microcanonical ensemble) with energy  $E$ , the entropy is defined in terms of the density of energy states

$$\exp\{S(E)\} = \sum_n \delta\{E - E_n\}.$$

Such a definition of the entropy is motivated by the fact that the number (density) of energy states generally grows exponentially with the number of degrees of freedom  $N$ , while the entropy must be extensive, i.e. proportional with  $N$ . For this function to be a smooth, analytic function of energy, one has to consider the thermodynamic limit  $N \rightarrow \infty$ , where

any discrete spectrum turns into a continuum one. [Note that for systems with a finite number of degrees of freedom and a discrete spectrum (e.g. a single quantum spin), this definition of  $S(E)$  does not make sense.]

Physically, we can say that the entropy measures the density of accessible states at a given energy. Now we can see the microscopic basis for the Second Law: in equilibrium all accessible states of a given energy tend to be equally populated, maximising the entropy.

Using this definition, we can rewrite the expression for the partition function as

$$Z(\beta) = \int d\varepsilon \exp\{S(\varepsilon)\} \exp\{-\beta\varepsilon\}.$$

it is interesting to examine this integral in the thermodynamic limit  $N \rightarrow \infty$ . Since  $S(\varepsilon) \rightarrow 0$  at  $\varepsilon \rightarrow 0$ , the integrand is dominated by a sharp peak at some  $\varepsilon = E(\beta)$ , which becomes increasingly sharper and sharper as  $N \rightarrow \infty$ , and the integral can be evaluated by a steepest descent method. To determine  $\varepsilon = E(\beta)$ , we look for the maximum of the integrand, and we find

$$\left. \frac{\partial S(\varepsilon)}{\partial \varepsilon} \right|_{\varepsilon=E(\beta)} = \beta.$$

We thus recover the relation between the microcanonical entropy and the temperature. To leading order (large  $N$ ), the partition function reduces to the integrand evaluated at the saddle point

$$Z(\beta) = \exp\{S(E(\beta)) - \beta E(\beta)\} = \exp\{-\beta F\},$$

the expected relation between the free energy and the entropy.