

# Contents

2	Thermodynamics	3
2.1	Some preliminary comments on forms	3
2.2	First law of thermodynamics	4
2.3	Zeroth law of thermodynamics	6
2.4	Second law of thermodynamics	7
2.4.1	Perpetua mobilia of second kind	7
2.4.2	Carnot engines	8
2.4.3	Absolute temperature	9
2.4.4	Absolute entropy	10
2.4.5	Gibbs' fundamental equation	12
2.4.6	Entropy of an ideal gas	13
2.5	Thermodynamic potentials	14
2.5.1	Conditions for equilibrium	14
2.5.2	Free energy	15
2.5.3	Convexity of extensive functions of state	16
2.5.4	A bit of convex geometry	18
2.5.5	Legendre transforms	19
2.5.6	Thermodynamic potentials	20
2.6	Phase transitions	23



## Chapter 2

# Thermodynamics

In this course, we will start by thermodynamical considerations, or rather with the field called phenomenological thermodynamics. As mentioned before, this field is closely related with statistical physics. Yet, it is not true that it has become totally obsolete by the advent of statistical physics. Partly for the mentioned reason that one does not want to keep track of the micro-state of every system. Partly also because some links between statistical physics and thermodynamics being still not quite fully understood (although I do not want to advocate a paranoid position here). There are some people who say that in the future, when our physical theories will look very different, thermodynamics will still be valid.

### 2.1 Some preliminary comments on forms

In this course, we will take a pragmatic attitude as far as mathematics is concerned. For example, we will consider small, “infinitesimal” changes of state variables. Formally, expressions of the type

$$\delta F = \sum_{j=1}^k F_j dG_j \quad (2.1)$$

are differential forms, in fact 1-forms, where the  $F_j, G_j : \mathcal{A} \rightarrow \mathbb{R}$  are differentiable functions in state space  $\mathcal{S}$ . We will not try to get too much side-tracked by considering geometric features here. It will be useful to view them as integrands of a line integral: We define

$$\int_C \delta F = \int_C \sum_{j=1}^k F_j dG_j = \int_I dt F_j(z(t)) \frac{d}{dt} G_j(z(t)). \quad (2.2)$$

The parametrization of the curve does not matter here.

For a scalar function  $G$  we call  $dG$  the differential of  $G$ . This is a special kind of differential form. In general, a differential form that is the differential

of a scalar is called an exact differential form. In particular, the integral then does not depend on the curve at all, and

$$\int_C dG = G(\text{End}) - G(\text{Beginning}). \quad (2.3)$$

(This differential form, applied to a vector field, gives the directional derivative in a point.)

If  $\mathcal{S}$  is  $n$ -dimensional and  $(x_1, \dots, x_n)$  form a coordinate system, then the functions  $F_j$  in the decomposition  $\delta F = \sum_{j=1}^n F_j dx_j$  are unique.

For an exact differential form, so for the differential of  $G$ , we have

$$dG = \sum_{j=1}^n \frac{\partial G}{\partial x_j} dx_j. \quad (2.4)$$

It should be clear that a partial derivative of the form  $\partial G / \partial x_j$  merely depends on  $G$  and the coordinate  $x_1$ , but in fact also of the other coordinates  $x_2, \dots, x_n$ . This is usually expressed as follows, writing

$$\left( \frac{\partial G}{\partial x_1} \right)_{x_2, \dots, x_n}. \quad (2.5)$$

One reads this as the “change of  $G$  with  $x_1$ , while holding  $x_2, \dots, x_n$  constant”.

If  $\delta F = \sum_{j=1}^n F_j dx_j$  is exact (so the differential of a scalar function), then one also has that

$$\left( \frac{\partial F_k}{\partial x_j} \right) = \left( \frac{\partial F_j}{\partial x_k} \right) \quad (2.6)$$

for all  $j, k$ , as follows from the interchangeability of the second derivatives. This condition is called integrability condition and form satisfying this is called closed. Hence, every exact form is closed. For simply connected state spaces, closed forms are also exact.

## 2.2 First law of thermodynamics

We consider a system with control parameters  $\alpha_1, \dots, \alpha_k$ . The energy given away by the system can be captured by (taken, in case of negative sign)

$$\delta A = \sum_j K_j d\alpha_j, \quad (2.7)$$

the work differential. For a simple gas, we have

$$\delta A = pdV, \quad (2.8)$$

with the volume  $V$  being the only control parameter. Other summands are  $MdB$  with magnetization  $M$  and induction  $B$ . Or  $\mu dN$  for chemical potential  $\mu$  and particle number  $N$ .

Note that work and heat are no state variables. Hence, they cannot be associated equilibrium states.

We now assume that the system is isolated from its environment, meaning that the change of energy is possible only by an alteration of the control parameters. One also says that the process is done in an adiabatic fashion. The first law of thermodynamics is the law of conservation of energy in such a situation.

First law of thermodynamics: Every thermodynamic system is associated a quantity inner energy  $U : \mathcal{S} \rightarrow \mathbb{R}$ . Along adiabatic curves in state space one has that

$$dU + \delta A = 0. \quad (2.9)$$

Except from applying work the inner energy can also be altered by exchange of heat. The heat flow  $\delta Q$  is

$$\delta Q = dU + \delta A. \quad (2.10)$$

The energy of an isolated system,  $\delta Q = 0$ ,  $\delta A = 0$ , is constant,  $dU = 0$ .

As an example, let us have a closer look at an ideal gas: The equation of state for the inner energy is

$$U = cpV, \quad (2.11)$$

with some constant  $c > 0$ . The work differential is  $\delta A = pdV$ . Hence,

$$0 = dU + \delta A = c(pdV + Vdp) + pdV = (c + 1)pdV + cVdp. \quad (2.12)$$

We now look at the adiabatic plane: This is the plane that be reached by a reversible and adiabatic, i.e.,  $\delta Q = 0$  process. Introducing the adiabatic coefficient

$$\kappa = \frac{c + 1}{c} \quad (2.13)$$

we get

$$0 = \kappa \frac{1}{V} dV + \frac{1}{p} dp = d(\kappa \ln V + \ln p) = d(\ln V^\kappa + \ln p), \quad (2.14)$$

that is to say, the adiabatic planes have to satisfy  $pV^\kappa$  is constant.

Since  $\delta A$  is no exact differential, the integral

$$\int_{\mathcal{C}} \delta A \quad (2.15)$$

depends on the parametrized curve, and is hence different from zero even for closed curves  $\mathcal{C}$ .

There is a simple consequence of the first law of thermodynamics. In fact, it is equivalent to the first statement of the above formulation of the first law of thermodynamics.

Impossibility of perpetual mobile of first kind: It is impossible to devise a periodically working machine delivering energy.

### 2.3 Zeroth law of thermodynamics

Experience teaches us that in thermodynamical systems, state variables such as temperature, inner energy and entropy play an important role. In the laws of thermodynamics these quantities are introduced in an axiomatic form. It is hence convenient to put at the beginning of this axiomatic framework the concept of temperature, in the zeroth law of thermodynamics.

We surely have the means, as humans, to judge to some extent whether two bodies have the same temperature. Such a notion can be made more precise as follows: If two systems are put into contact with each other, a equilibration of the energy will take place, in a way such that the total energy  $U = U^{(1)} + U^{(2)}$  is conserved. We say that two systems are in thermal equilibrium, if no such distribution of energy takes place.

Zeroth law of thermodynamics: Thermal equilibrium is an equivalence relation.

These equivalence classes can be parametrized by means of the state of a suitable test system. A function  $\hat{T} : \mathcal{S} \rightarrow \mathbb{R}$  is called empirical temperature if

$$\hat{T}(z_1) = \hat{T}(z_2) \tag{2.16}$$

exactly if  $z_1$  and  $z_2$  are in thermal equilibrium. Using the zeroth law of thermodynamics, these scales are usable for different kinds of thermodynamical systems. So in a sense, this law merely says that “temperature exists”, but is unspecific about the precise scale that is being used.

Two systems that are in contact give rise to a new thermodynamic system. If the parts have  $k^{(1)}$  and  $k^{(2)}$  control parameters, so if the state spaces are  $k^{(1)} + 1$  and  $k^{(2)} + 1$  dimensional, then the joint system has

$$k^{(1)} + k^{(2)} \tag{2.17}$$

control parameters. The inner energies of each part are no longer independent variables, but only the total energy  $U = U^{(1)} + U^{(2)}$ . So again, in addition to the control parameters, a single parameter is required to define the system’s state, and again the system is simple.

## 2.4 Second law of thermodynamics

### 2.4.1 Perpetua mobilia of second kind

We now turn to the second law of thermodynamics. We consider systems that are composed of several simple thermodynamic systems. Some of those systems may be so large that they hardly change their state when they are brought into contact with small systems. Such systems are called heat baths. What is more, the joint system should embody a reservoir for mechanical work.

We assume that it is possible to bring parts into contact with each other and to also interrupt this contact, at free will. On top of the processes that are resulting from parts coming to equilibrium, we allow for those processes that are a result of us changing the control parameters in the subsystems.

It is clear, from the first law of thermodynamics, that the total energy of the system has to be preserved: The reservoir for mechanical work can not be loaded up without changing the rest of the system. In this sense, mechanical work cannot be created from nothing. This would indeed be a perpetual mobile of first kind.

A perpetual mobile of second kind is a device or a process that is able to load the reservoir of mechanical work, but at the expense of only the inner energy of one of the subsystems, but without any change to any of the other subsystems. The second law of thermodynamics states that this does not exist:

Second law of thermodynamics (Planck's formulation): A perpetual mobile of second kind does not exist.

There is a simple yet very important consequence of this law, when applied to a single simple system. We consider an adiabatic process in which control parameters are changed in a circular process. In the course of this process, the alteration of the inner energy  $dU$  can be read off the condition  $0 = \delta Q = dU + \delta A$  and integrated up. So let us compare the inner energies  $U(0)$  and  $U(1)$  at the beginning and at the end of the process. If we had

$$U(1) < U(0), \tag{2.18}$$

we would have done work on the basis of only using up inner energy, which is forbidden by the second law of thermodynamics. If in contrast,

$$U(0) < U(1), \tag{2.19}$$

the same would be true for the process run in the converse direction. That is to say,  $U(0) = U(1)$ . The curves with fixed beginning and end point and  $\delta Q$  span indeed a plane in  $\mathcal{S}$ , adiabatic planes. Now there exists a function  $\hat{S} : \mathcal{S} \rightarrow \mathbb{R}$ , the planes of constant values are exactly the adiabatic planes. This function is called empirical entropy.

The observation that is behind this concept of entropy is that real processes in nature are usually irreversible. When a hot body and a cold one is put into contact with each other, they will equilibrate. Never it is observed that one part becomes even colder whereas the hotter body becomes hotter still. Or, if a stone is thrown into a pool, the pool will become a little bit warmer and the stone will sink to the ground. It is never observed that a stone is jolting out of the surface of a pool, while the water cools down. These processes would not be in contradiction with the first law of thermodynamics, though. It is the second law of thermodynamics that forbids them. Real processes are irreversible. And it is the entropy that captures that irreversibility. We will say more about the interpretation of the entropy in a minute.

### 2.4.2 Carnot engines

A Carnot process is a circular process involving a simple system that consists of four steps in contact with two heat baths at empirical temperatures  $\hat{T}_+$  and  $\hat{T}_-$ . At the beginning, the system has an empirical entropy  $\hat{S}_-$  and an empirical temperature  $\hat{T}_+$ .

Steps of the Carnot process:				
Step	Contact with	Entropy	Heat exchange	Work done
1	$\hat{T}_+$		$Q_1 > 0$	$A_1$
2		$\hat{S}_+$		$A_2$
3	$\hat{T}_-$		$Q_3 < 0$	$A_3$
4		$\hat{S}_-$		$A_4$

We are not so much concerned with the details of the process, but rather that isothermal and adiabatic steps follow each other, at the respective empirical temperatures and entropies. Also, the end state at  $\hat{T}_+$  and  $\hat{S}_-$  should be identical with the state at the beginning.

Now note that an isothermal process is in fact nothing but an adiabatic process of the system and the heat bath it is in contact with. Therefore, we can – just as for an adiabatic process – run the process in the converse direction, where the signs of  $Q_i$  and  $A_i$  then change. Because

$$0 = \int_{\mathcal{C}} dU = \sum_j Q_j - \sum_j A_j \quad (2.20)$$

is

$$Q_1 + Q_3 = A := \sum_j A_j, \quad (2.21)$$

where  $A$  is the work done in total. Because of the second law of thermodynamics the signs of  $Q_1$  and  $Q_3$  have to be different. Since in step 1 the empirical



temperature is higher,

$$Q_1 > 0 > Q_3 \quad (2.22)$$

and we expect  $Q_1 + Q_3 > 0$ . In the given direction, the machine is hence a heat engine (getting work done from heat), whereas run in the converse direction is a heat pump (getting a temperature difference using work). An important property of Carnot processes is the following one:

Efficiency of the Carnot engine: For all Carnot processes run at empirical temperatures  $\hat{T}_+ > \hat{T}_-$  the ratio

$$\frac{|Q_3|}{Q_1} \quad (2.23)$$

is the same. The efficiency of a heat engine is the quotient

$$\eta = \frac{\text{Work done}}{\text{Heat taken up}} = \frac{-(Q_1 + Q_3)}{Q_1} = 1 - \frac{|Q_3|}{Q_1}. \quad (2.24)$$

That is to say, all Carnot engines have the same efficiency. The idea of the proof is as follows: Surely the only thing that can matter is the ratios of the  $Q_i$  as we can run each process several times. We can hence assume that we have two processes, and that  $Q'_1 = Q_1$ . If now  $A' < A$  was true, so if the new machine could do less work, and hence  $Q'_3 > Q_3$ , then we could run the new process as a heat pump and would have a new total process, delivering the work  $A - A' > 0$ , only at the expense of taking the heat  $Q_3 - Q'_3$  from the colder reservoir. This is in contradiction with the second law.

### 2.4.3 Absolute temperature

According to the above observation,

$$f(\hat{T}_+, \hat{T}_-) = \frac{|Q_3|}{Q_1} \quad (2.25)$$

is a well-defined function of the empirical temperatures. If we now have three heat baths, at empirical temperatures

$$\hat{T}_+ > \hat{T}_0 > \hat{T}_- \quad (2.26)$$

we can compose suitable Carnot processes between  $\hat{T}_+$  and  $\hat{T}_0$  (with heat exchange  $Q'_1$  and  $Q'_3$ ) as well as between  $\hat{T}_0$  and  $\hat{T}_-$  (with heat exchange  $Q_1$  and  $Q_3$ ) to a new process. We run it in a way that step 1 of the process at lower temperature is the reverse of step 3 of the process at higher temperature. That is,

$$Q'_3 = -Q_1. \quad (2.27)$$

We can hence simply not do that step. The composed process has

$$Q_1'' = Q_1', \quad (2.28)$$

$$Q_3'' = Q_3. \quad (2.29)$$

Therefore,

$$f(\hat{T}_+, \hat{T}_-) = \frac{|Q_3''|}{Q_1''} = \frac{|Q_3|}{Q_1} \frac{|Q_3'|}{Q_1'} = f(\hat{T}_0, \hat{T}_-)f(\hat{T}_+, \hat{T}_0). \quad (2.30)$$

From this, we get an absolute temperature scale! For a randomly picked empirical temperature  $\hat{T}_0$  we fix some value  $T_0$ . This could be the value 273.15, but this is obviously just a convention. Then we define

$$T(\hat{T}) = f(\hat{T}_0, \hat{T})\hat{T}_0. \quad (2.31)$$

This is called the absolute temperature. The possibility of choosing  $\hat{T}_0$  amounts to the fact that the absolute temperature has some dimension. Here, we get the Kelvin scale, needless to say.

Using the definition of the absolute temperature, we get

$$f(\hat{T}_+, \hat{T}_-) = \frac{T(\hat{T}_-)}{T(\hat{T}_+)} = \frac{T_-}{T_+}, \quad (2.32)$$

and hence for the efficiency of the Carnot engine

$$\eta = 1 - \frac{T_-}{T_+}. \quad (2.33)$$

Since the empirical temperature was a random choice anyway related to picking representatives of equivalence classes, we will from now on use the absolute temperature only.

#### 2.4.4 Absolute entropy

We can continue with our effort of making quantities “absolute” and can think of a notion of the absolute entropy. We fix an adiabatic plane and call its entropy  $S_0$ . For another adiabatic plane we pick the value

$$S = S_0 + \frac{1}{T} \int_{\mathcal{C}} \delta Q, \quad (2.34)$$

where  $\mathcal{C}$  is some path that connects the reference plane to the new adiabatic plane. This definition does not depend on the chosen path, as follows from our above observation of Carnot processes: Two different paths we could, with many appropriate adiabatic pieces, connect to a Carnot engine, so that the integrals in both entropy definitions would become the heat values  $Q_1$  and  $Q_3$ . We call the above quantity the absolute entropy.

We can even simplify our expression of the absolute entropy. Surely  $\delta Q$  and  $dS$  will vanish on the adiabatic steps. Hence, there must be some integrating factor  $\lambda$  with  $dS = \lambda\delta Q$ . This factor we can determine along any isothermal path, and find from Eq. (2.34)  $\lambda = 1/T$ . Hence,

$$dS = \frac{\delta Q}{T}. \quad (2.35)$$

We can hence compute  $S$  as a line integral of  $\delta Q/T$  over an arbitrary path.

We can now define the total entropy of a composite quantum system as the sum of the entropies of the parts. This definition is perfectly compatible with the composition of parts under heat contact. Since  $U = U^{(1)} + U^{(2)}$  and since the control parameters are the sum of the control parameters of the parts,

$$\delta A = \delta A^{(1)} + \delta A^{(2)}. \quad (2.36)$$

Therefore

$$\delta Q = \delta Q^{(1)} + \delta Q^{(2)}. \quad (2.37)$$

and since in contact with a heat bath the temperature is held constant,

$$dS = \frac{1}{T}\delta Q = dS^{(1)} + dS^{(2)}. \quad (2.38)$$

It is clear that this total entropy is conserved as long as merely adiabatic processes take place in its parts. Also, for the Carnot process, the total entropy of system and its bath is conserved.

Another consequence of the second law of thermodynamics is that if two systems at different temperatures are put into contact with each other, the energy can only spontaneously flow from the hotter to the colder body. Otherwise, one could gain work from a subsequent Carnot engine. If two systems at temperatures  $T_+ > T_-$  are put into contact, hence  $\delta Q_- = -\delta Q_+ > 0$ , and therefore

$$dS = dS^{(1)} + dS^{(2)} = \frac{\delta Q_-}{T_-} + \frac{\delta Q_+}{T_+} = \delta Q_- \left( \frac{1}{T_-} - \frac{1}{T_+} \right) > 0. \quad (2.39)$$

Since every process we considered is either isothermal or adiabatic, this means that the entropy can only grow.

Processes that do not involve steps of spontaneous heat exchange between parts of different temperature, but merely adiabatic processes of composite systems, can be reversed by reversing the switching of the control parameters. They are hence reversible and satisfy  $dS = 0$ . Also, one can show that every change of state with  $dS = 0$  can be reached in this fashion. Processes with  $dS > 0$  are hence exactly the irreversible processes. In fact, this observation, which is here a consequence of the laws as we introduced them, is usually referred to as the Sommerfeld formulation of the second law of thermodynamics.

Second law of thermodynamics (Sommerfeld's formulation): Every system has an extensive quantity  $S$ , the entropy. Its change in reversible processes is obtained by taking the added heat and dividing it by the temperature at which this process is performed. In all irreversible processes, inner entropy is being generated.

Often, one writes the balance in the change of entropy as

$$dS = d_i S + d_e S, \quad (2.40)$$

meaning that the entropy can change either by it being altered in the system itself ( $d_i S$ ), or by a flow of entropy to or out of the system  $d_e S$ . A way of putting this irreversibility is that

$$d_i S \geq 0. \quad (2.41)$$

The entropy exchanged  $d_a S$  with a heat bath and the heat  $\delta Q$  that is exchanged at temperature  $T$  in a reversible fashion is

$$d_a S = \frac{1}{T} \delta Q. \quad (2.42)$$

The above statements

$$dS = d_a S + d_i S \quad (2.43)$$

and

$$d_a S = \frac{\delta Q}{T}, \quad d_i S \geq 0 \quad (2.44)$$

are combined to

$$dS \geq \frac{\delta Q}{T}. \quad (2.45)$$

#### 2.4.5 Gibbs' fundamental equation

We now want to combine the first and the second laws in a single expression. We find for reversible processes

$$dS = \frac{1}{T} dU - \frac{1}{T} \delta A. \quad (2.46)$$

Writing  $\delta A$  as

$$\delta A = \sum_j K_j d\alpha_j, \quad (2.47)$$

we have the following:

Gibbs' fundamental equation:

$$dS = \frac{1}{T}dU - \frac{1}{T} \sum_j K_j d\alpha_j. \quad (2.48)$$

### 2.4.6 Entropy of an ideal gas

Let us as an example consider a simple ideal gas, defined as a substance for which the isothermals are of the form  $pV = \theta$  (const), and the inner energy of which is

$$U = \frac{f}{2}\theta. \quad (2.49)$$

We can express the differential form  $dS$  in the coordinate system  $(\theta, V)$ ,

$$dS = \frac{f}{2T}d\theta + \frac{\theta}{VT}dV. \quad (2.50)$$

Since this is a closed differential form, and since  $T$  merely depends on  $\theta$ , we have to have

$$0 = \left( \frac{\partial(f/(2T))}{\partial V} \right)_\theta = \left( \frac{\partial(\theta/(TV))}{\partial \theta} \right)_V. \quad (2.51)$$

This means that

$$\lambda := \frac{\theta}{T} \quad (2.52)$$

is independent of  $\theta$ . Using this fact, we get

$$dS = \lambda \left( \frac{f}{2} \frac{dT}{T} + \frac{dV}{V} \right), \quad (2.53)$$

and therefore,

$$S(T, V) = S_0 + \lambda \left( \frac{f}{2} \ln \frac{T}{T_0} + \ln \frac{V}{V_0} \right). \quad (2.54)$$

Using the relation

$$U = \frac{f}{2}\lambda T, \quad (2.55)$$

we can in the variables  $(U, V)$  express this also as

$$S(U, V) = S_0 + \lambda \left( \frac{f}{2} \ln \frac{U}{U_0} + \ln \frac{V}{V_0} \right). \quad (2.56)$$

This is the desired expression of the entropy of the ideal gas.

## 2.5 Thermodynamic potentials

### 2.5.1 Conditions for equilibrium

If two simple systems are brought into contact with each other, they will arrive at an equilibrium state at some temperature  $T^{(1)} = T^{(2)}$ . If the systems are initially not in equilibrium, then the final state reached will depend on the specifics of how this equilibrium is reached. In particular, it will depend on whether mechanical work is being generated or not. If the temperature equilibration happens spontaneously, then the entropy will increase, as explained above, until the state maximum entropy given the fixed total energy has been reached. In case that when reaching equilibrium work is being performed using reversibly operating heat engines, then the entropy will be constant, and the inner energy will change, until equilibrium is reached.

Let us first look at the situation of maximising the entropy under fixed control parameters. Denoting all quantities of one container with (1) and the other with (2), we have

$$dS = dS^{(1)} + dS^{(2)} = \frac{1}{T^{(1)}} dU^{(1)} + \frac{1}{T^{(2)}} dU^{(2)} = \left( \frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU_1 \geq 0, \quad (2.57)$$

which means that in equilibrium,

$$T^{(1)} = T^{(2)}. \quad (2.58)$$

Also, if we maximise the inner energy when holding the entropy constant at fixed control parameters, again

$$dU = dU^{(1)} + dU^{(2)} = T^{(1)} dS^{(1)} + T^{(2)} dS^{(2)} = (T^{(1)} - T^{(2)}) dS^{(1)} \quad (2.59)$$

from which again  $T^{(1)} = T^{(2)}$  follows in equilibrium.

In this discussion, we have assumed that the control parameters are static. We can also look at equilibrium values in situations where we can tune the control parameters appropriately, using the method of Lagrange parameters<sup>1</sup>. For example, let us think of two containers that are coupled via a movable object, in a way that

$$\frac{V^{(1)}}{a_1} + \frac{V^{(2)}}{a_2} = \text{const}. \quad (2.63)$$

---

<sup>1</sup>In general, consider functions  $f, g_1, \dots, g_J : \mathbb{R}^n \rightarrow \mathbb{R}$ . If one wants to solve the problem

$$\min \quad f(\mathbf{x}), \quad (2.60)$$

$$\text{subject to} \quad g_j(\mathbf{x}) = c_j, \quad (2.61)$$

$j = 1, \dots, J$ , then one can look at the stationary points with  $dL = 0$  of the Lagrangian

$$L(\mathbf{x}, \lambda) = f(\mathbf{x}) - \sum_{j=1}^J \lambda_j (g_j(\mathbf{x}) - c_j). \quad (2.62)$$

Under technical conditions (the constraint qualification conditions), then necessary for points to solve the above problem for  $f$  under the constraints given by  $g_1, \dots, g_J$  is that the point is stationary.

If we release this system in a non-equilibrium initial condition, then we will encounter some oscillations. Eventually, by means of irreversible dynamics, these oscillations will be dampened, generating entropy, until the maximum is reached. We can also shift the initial potential energy to a reservoir for mechanical work, until no longer a force acts onto the movable object. The equilibrium condition is hence that  $U$  is extremal, under the three constraints

$$\frac{V^{(1)}}{a_1} + \frac{V^{(2)}}{a_2} = \text{const}, \quad (2.64)$$

$$S^{(1)} = \text{const}, \quad (2.65)$$

$$S^{(2)} = \text{const}. \quad (2.66)$$

The two entropies will be held constant separately, since we think of both parts of the system being thermally isolated. The inner energies of the two parts are

$$dU^{(i)} = T^{(i)}dS^{(i)} - p^{(i)}dV^{(i)}, \quad (2.67)$$

with  $dU = dU^{(1)} + dU^{(2)}$ . With the Lagrange parameters  $\lambda, \lambda_1, \lambda_2$  we get

$$\begin{aligned} 0 &= dU - \lambda_1 dS^{(1)} - \lambda_2 dS^{(2)} - \lambda d(V^{(1)}/a_1 + V^{(2)}/a_2) \\ &= (T^{(1)} - \lambda_1)dS^{(1)} + (T^{(2)} - \lambda_2)dS^{(2)} \\ &\quad - \left(p^{(1)} + \frac{\lambda}{a_1}\right)dV^{(1)} - \left(p^{(2)} + \frac{\lambda}{a_2}\right)dV^{(2)}. \end{aligned} \quad (2.68)$$

Now these two differentials are linearly independent. Hence, solving for  $\lambda$  gives that we have to have

$$p^{(1)}a_1 = p^{(2)}a_2. \quad (2.69)$$

In particular, when  $a_1 = a_2 = 1$ , then the condition for equilibrium is simply

$$p^{(1)} = p^{(2)}, \quad (2.70)$$

and the pressure has to be the same on both sides.

### 2.5.2 Free energy

Let us move on by considering a simple system in contact with a heat bath at temperature  $T_B$ . The control parameters  $\alpha_1, \dots, \alpha_k$ , such as in the last example the volumes, may be subject to any kind of constraints. The index  $B$  labels the heat bath in this case. In order to keep things simple, let us take as coordinates in state space the control parameters as well as the entropy (remember that for simple systems, the dimension of state space is one more than the number of control parameters). We aim at finding the minimum of the inner energy  $U + U_B$  for fixed entropy  $S + S_B$  and other constraints.

We can compute the minimum in two steps. We first hold the control parameters constant and vary the distribution of entropy between system and bath. Since

$$dU_B = T_B dS_B = -T_B dS, \quad (2.71)$$

with  $T_B$  not being dependent on the state (it is a heat bath, after all), this first step amounts to finding the minimum of  $U - T_B S$ . We define the free energy as

$$F(T_B, \alpha_1, \dots, \alpha_k) = \min \{U - T_B S : (\alpha_1, \dots, \alpha_k) \text{ fixed}\}. \quad (2.72)$$

If we consider the inner energy  $U$  as a function of  $(S, \alpha_1, \dots, \alpha_k)$ , we merely have to find the value of  $S$  for which the minimum is attained. At this point we also have  $T = T_B$ , surely, so that we can write

$$F = U - TS. \quad (2.73)$$

By introducing the free energy  $F$ , the variables of the bath are eliminated, with the exception of  $T_B$ , and we only have to find the minimum of  $F(T_B, \alpha_1, \dots, \alpha_k)$ , respecting the possibly available constraints to the control parameters  $\alpha_1, \dots, \alpha_k$ .

### 2.5.3 Convexity of extensive functions of state

If we increase the “magnitude” of a homogeneous material by a factor of  $\lambda$ , then one transforms a system with extensive variables  $S, U, V, N$  into one with variables  $\lambda S, \lambda U, \lambda V, \lambda N$ . Here,  $N$  can stand for the particle number, and more generally the vector  $\mathbf{N}$  of particle numbers of particles of different kinds. The function that determines the inner energy, therefore, satisfies

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N). \quad (2.74)$$

Such functions are also called homogeneous of grade 1. Differentiating this function and then setting  $\lambda = 1$ , one obtains

$$\left(\frac{\partial U}{\partial S}\right) S + \left(\frac{\partial U}{\partial V}\right) V + \sum_{i=1}^s \left(\frac{\partial U}{\partial N_i}\right) N_i = U. \quad (2.75)$$

These partial derivatives have already been identified earlier when discussing work differentials and the definition of the entropy. We have

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial S}\right) dS + \left(\frac{\partial U}{\partial V}\right) dV + \sum_{i=1}^s \left(\frac{\partial U}{\partial N_i}\right) dN_i \\ &= TdS - pdV + \sum_{i=1}^s \mu_i dN_i. \end{aligned} \quad (2.76)$$

The variables  $\mu_i$ ,  $i = 1, \dots, s$ , are called chemical potentials. Since  $S, V, \mathbf{N}$  form a coordinate system, the coefficients of the differentials are uniquely determined, so

$$T = \left(\frac{\partial U}{\partial S}\right)_{V, \mathbf{N}} \quad (2.77)$$

and so on. In this way, we get from Eq. (2.75) the following equation.



Gibbs-Duhem equation:

$$U = TS - pV + \sum_{i=1}^s \mu_i N_i. \quad (2.78)$$

Finally, we can also come up with an expression for the entropy of an ideal gas as a function of the number of particles of a single kind  $N$ , using the expression

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N). \quad (2.79)$$

We can take  $N = \lambda N_0$  where  $N_0$  is the number of particles for which we have computed the entropy above, in Eq. (2.56). This way, we get the following equation.

Sackur-Tetrode-equation:

$$S(U, V, N) = N \left( \frac{f}{2} \ln \frac{U}{U_0} + \ln \frac{V}{V_0} - \frac{f+2}{f} \ln \frac{N}{N_0} + \frac{S_0}{N_0} \right). \quad (2.80)$$

By means of differentiation to  $U$  and  $V$ , respectively, one gets

$$U = \frac{f}{2} NT, \quad pV = NT. \quad (2.81)$$

The numbers  $N_0$ ,  $V_0$ , and  $U_0$  here merely reflect the units.

What happens now if we put two systems into heat contact with another, the extensive quantities of which are not proportional? Let us assume that the parts are described by inner energy functions  $U^{(1)}$  and  $U^{(2)}$ , the joint system by the function  $U^{(12)}$ . We start with an initial state in which the parts are described by  $S^{(i)}$ ,  $V^{(i)}$ , and  $\mathbf{N}^{(i)}$ . By means of adiabatic processes, for which

$$S = S^{(1)} + S^{(2)} \quad (2.82)$$

is held constant, one draws energy from the system, until it is in equilibrium. Here, merely the joint volume

$$V = V^{(1)} + V^{(2)} \quad (2.83)$$

is thought to be constrained, and no particles should be generated or destroyed,  $\mathbf{N} = \mathbf{N}^{(1)} + \mathbf{N}^{(2)}$ . The equilibrium states of the joint system is hence described by  $U, V, \mathbf{N}$ , and it is

$$U^{(12)}(S, V, \mathbf{N}) \leq U^{(1)}(S^{(1)}, V^{(1)}, \mathbf{N}^{(1)}) + U^{(2)}(S^{(2)}, V^{(2)}, \mathbf{N}^{(2)}). \quad (2.84)$$

The inequality originates from the fact that also work could have been done. We assume that both systems are homogeneous systems, so contain only one kind of particles, the three functions  $U^{(1)}$ ,  $U^{(2)}$ , and  $U^{(12)}$  are in fact the same, and therefore,

$$U(S^{(1)}+S^{(2)}, V^{(1)}+V^{(2)}, \mathbf{N}^{(1)}+\mathbf{N}^{(2)}) \leq U(S^{(1)}, V^{(1)}, \mathbf{N}^{(1)})+U(S^{(2)}, V^{(2)}, \mathbf{N}^{(2)}). \quad (2.85)$$

One also says that the function  $U$  is sub-additive. Similarly, replacing the principle of minimal energy by the maximum entropy principle, one arrives at

$$S(U^{(1)}+U^{(2)}, V^{(1)}+V^{(2)}, \mathbf{N}^{(1)}+\mathbf{N}^{(2)}) \geq S(U^{(1)}, V^{(1)}, \mathbf{N}^{(1)})+S(U^{(2)}, V^{(2)}, \mathbf{N}^{(2)}) \quad (2.86)$$

that is to say, the entropy function is super-additive. Any function that is sub additive and homogeneous of grade one is also convex: This means that for any  $\lambda \in [0, 1]$ ,

$$\begin{aligned} & U(\lambda S^{(1)} + (1 - \lambda)S^{(2)}, \lambda V^{(1)} + (1 - \lambda)V^{(2)}, \lambda \mathbf{N}^{(1)} + (1 - \lambda)\mathbf{N}^{(2)}) \\ & \leq \lambda U(S^{(1)}, V^{(1)}, \mathbf{N}^{(1)}) + (1 - \lambda)U(S^{(2)}, V^{(2)}, \mathbf{N}^{(2)}). \end{aligned} \quad (2.87)$$

For  $S$ , the converse inequality is true, that is, i.e., it is a convace function. These properties may be seen as stability conditions. One can gain work by turning a non-homogeneous state into a homogeneous one.

#### 2.5.4 A bit of convex geometry

Let us do a bit of a detour and have a look at convex functions and sets. This is educational anyway. But in this way, we will also understand the role of Legendre transforms in thermodynamics. A set  $S \subset \mathbb{R}^n$  is called convex if the line segment connecting any two elements is also contained in the set, that is,

$$\lambda \mathbf{x} + (1 - \lambda)\mathbf{y} \in S \quad (2.88)$$

for all  $x, y \in S$ . A function  $f : \mathbb{R}^n \rightarrow \mathbb{R}$  is called convex, if

$$f\left(\sum_i \lambda_i \mathbf{x}_i\right) \leq \sum_i \lambda_i f(\mathbf{x}_i), \quad (2.89)$$

for

$$\lambda_i \geq 0, \quad \sum_i \lambda_i = 1. \quad (2.90)$$

Such functions are actually called convex, because their supergraph is a convex set, that is, the set

$$\{(\mathbf{x}, y) \in \mathbb{R}^n \times \mathbb{R} : y \geq f(\mathbf{x})\} \subset \mathbb{R}^{n+1} \quad (2.91)$$

is convex. It is sufficient to check the above inequality for two summands with  $\lambda_1 + \lambda_2 = 1$ , the general statement follows from induction. It is also convenient

to allow for function values  $\infty$  and write  $\bar{\mathbb{R}}$  for  $\mathbb{R} \cup \infty$ . Again,  $f$  is concave if  $-f$  is convex. A function is both convex and concave, if it is an affine function, so if  $f$  is of the form

$$f(x) = \xi \cdot \mathbf{x} - c, \quad (2.92)$$

where  $c \in \mathbb{R}$ ,  $\xi \in \mathbb{R}^n$ , and the dot stands for the standard scalar product. The pointwise supremum of an arbitrary collection of convex functions is convex.

A twice differentiable function  $f : \mathbb{R} \rightarrow \mathbb{R}$  is convex exactly if  $f''(\mathbf{x}) \geq 0$  for all  $\mathbf{x}$ . For functions of many variables, it is sufficient to look at the directional derivative along arbitrary lines. This is equivalent with the positive-definiteness of the matrix  $M$  with entries

$$M_{j,k} = \frac{\partial^2 f}{\partial x_j \partial x_k}(\mathbf{x}). \quad (2.93)$$

This means that this function has non-negative eigenvalues only. For this, needless to say, one needs that the function is twice differentiable.

### 2.5.5 Legendre transforms

For every set  $K \subset \mathbb{R}^n$  there is a smallest convex set  $S \supset K$  that contains  $K$ . This is called the convex hull of  $K$ , denoted as  $\text{co}(K)$ . Via the supergraph construction,  $\text{co}f$  is the largest convex function that is smaller than  $f$ .

In order to make sure that  $\text{co}f$  exists, we have to know that there is an affine function that bounds  $f$  from below. We now look for a fixed  $\xi$  the largest affine function that is below  $f$ . The condition

$$f(\mathbf{x}) \geq l(\mathbf{x}) = \xi \cdot \mathbf{x} - c \quad (2.94)$$

for all  $\mathbf{x}$  is equivalent with

$$c \geq \xi \cdot \mathbf{x} - f(\mathbf{x}). \quad (2.95)$$

Legendre transform:

$$c \geq \tilde{f}(\xi) := \sup_{\mathbf{x}} \{ \xi \cdot \mathbf{x} - f(\mathbf{x}) \}. \quad (2.96)$$

The function  $\tilde{f} : \mathbb{R}^n \rightarrow \bar{\mathbb{R}}$  is called Legendre transform of  $f$ .

The function  $\tilde{f}$  is convex, as a supremum of affine functions. In fact,

$$\text{co}f(\mathbf{x}) = \sup_{\xi} \{ \xi \cdot \mathbf{x} - \tilde{f}(\xi) \} = \tilde{\tilde{f}}(\mathbf{x}). \quad (2.97)$$

If  $f$  was convex in the first place, of course  $\tilde{\tilde{f}} = f$ . These Legendre transforms will play a role in a minute, when we discuss thermodynamic potentials.

## 2.5.6 Thermodynamic potentials

Thermodynamic potentials are functions which contain the complete information about the thermostatic properties of a system. The for our purposes most important such functions are  $U(S, V, N)$ , the free energy  $F(T, V, N)$ , the enthalpy  $G(T, p, N)$ , which we will encounter in a minute, the grand canonical potential  $J(T, V, \mu)$ , which we will also learn about soon. We do not mean the state variables of the same name, but really the full functions of the respective variables. Each of the potentials describes under appropriate conditions the work done by the system, hence we will find an extremal principle, which will correspond to certain convexity properties.

The best studied function of this type so far is the inner energy. The differential of the inner energy is

$$dU = TdS - pdV + \sum_{i=1}^s \mu_i N_i = TdS - \delta A. \quad (2.98)$$

Since  $(S, V, \mathbf{N})$  is a coordinate system, we find, or rather have found already,

$$T(S, V, \mathbf{N}) = \left( \frac{\partial U}{\partial S} \right)_{V, \mathbf{N}}, \quad (2.99)$$

$$p(S, V, \mathbf{N}) = - \left( \frac{\partial U}{\partial V} \right)_{S, \mathbf{N}}, \quad (2.100)$$

$$\mu_i(S, V, \mathbf{N}) = \left( \frac{\partial U}{\partial N_i} \right)_{S, V}. \quad (2.101)$$

From the first relations we can by elimination of  $S$  get the pressure  $p$  as a function of  $(T, V, \mathbf{N})$ . As we know from the ideal gas, the knowledge of  $p(T, V, \mathbf{N})$  is not enough to reconstruct  $U$ , as the parameter  $f$  remains uncertain. This function is hence not a thermodynamical potential in our sense.

In adiabatic processes with  $dS = 0$  we have  $dU = -\delta A$ . This we have put into relationship with a minimality principle for energy. The point was as follows: Given two systems that are each in equilibrium, but not with each other. Then we can draw work from the joint system in an adiabatic fashion (under the given constraints) until equilibrium has been reached. In equilibrium hence  $U$  becomes minimal for an adiabatically isolated joint system. From this, we have concluded the convexity of the function

$$(S, V, \mathbf{N}) \mapsto U(S, V, \mathbf{N}). \quad (2.102)$$

This, in turn, leads to inequalities for the second derivatives of  $U$ , so the first derivatives of  $T, p, \mu_1, \dots, \mu_s$ . For example,

$$\left( \frac{\partial p}{\partial V} \right)_{S, \mathbf{N}} = - \left( \frac{\partial^2 U}{\partial V^2} \right)_{S, \mathbf{N}} \leq 0. \quad (2.103)$$

In the  $p$ - $V$ -diagram adiabatic curves with  $S$  being constant hence have a negative slope. So again, we get statements on the shape of adiabatic curves from the convexity of the inner energy function.

We now turn to the free energy. We have defined it as

$$\begin{aligned} F(T_B, V, \mathbf{N}) &= \inf_S \{U(S, V, \mathbf{N}) - T_B S\} = -\sup_S \{T_B S - U(S, V, \mathbf{N})\} \\ &= -\left(\tilde{U}(\cdot, V, \mathbf{N})\right)(T_B). \end{aligned} \quad (2.104)$$

Up to the sign, this is hence the Legendre transform of  $U$  as a function of  $S$ , at constant  $V$  and  $\mathbf{N}$ . Since we can from  $F$  determine  $U$  again by a Legendre transform, since it is convex (for convex functions, the “double Legendre transform is the function itself”), it is clear that  $F$  – just as well as  $U$  – must contain the complete information about the thermodynamic system. Since the infimum of  $F$  is obtained by definition at the temperature

$$T_B = \left(\frac{\partial U}{\partial S}\right)_{V, \mathbf{N}} = T, \quad (2.105)$$

one has

$$F = U - TS, \quad (2.106)$$

hence

$$\begin{aligned} dF &= dU - TdS - SdT = -\delta A - SdT \\ &= -SdT - pdV + \sum_{i=1}^s \mu_i dN_i, \end{aligned} \quad (2.107)$$

using the familiar expression of the work differential. We have taken  $(T, V, \mathbf{N})$  as the coordinate system, so can again consider the partial derivatives to “their” variables.

In order to compute the free energy for an ideal gas, say, one can eliminate the inner energy in the expression  $F = U - TS$  by using  $S$  as in Eq. (2.80) and

$$U = \frac{f}{2} NT. \quad (2.108)$$

In this way, one obtains

$$F(T, V, N) = NT \left( \frac{f}{2} \left( 1 - \ln \frac{T}{T_0} \right) - \ln \frac{V}{V_0} + \ln \frac{N}{N_0} - \frac{S_0}{N_0} \right). \quad (2.109)$$

In case a process is performed in an isothermal fashion, in contact with a bath of temperature  $T$ , then  $dT = 0$ , so

$$dF = -\delta A. \quad (2.110)$$

Along isothermal paths in state space, one can hence integrate the work done to  $F(T, \text{End}) - F(T, \text{Beginning})$ . We again arrive at an extremity principle:

We can bring two parts together, both of which are in contact with the same heat bath. If we allow – under appropriate constraints – the variation of the parameters  $V^{(i)}$  and  $\mathbf{N}^{(i)}$ , then a new equilibrium will be reached. We can arrive at this equilibrium by taking out as much energy as possible (see the above work differential). Since this happens in an isothermal fashion, we have to find the state of minimal free energy, given the constraints. In a way, the free energy is constructed to just capture such isothermal situations.

We also find that  $F$  has to be subadditive as a function of  $V$  and  $\mathbf{N}$ . Using the homogeneity (of the function), again again the argument that we can draw work from the system until the free energy is minimal, we find that  $(V, \mathbf{N}) \mapsto F(T_B, V, \mathbf{N})$  has to be a convex function, at fixed  $T$ . A simple consequence of the convexity of  $F$  is

$$\left(\frac{\partial p}{\partial V}\right)_{T, \mathbf{N}} = -\left(\frac{\partial^2 F}{\partial V^2}\right)_{T, \mathbf{N}} \leq 0. \quad (2.111)$$

The isothermal lines in the  $p$ - $V$ -diagram hence have, just as the adiabatic lines, a negative slope. Again, this is a quite sophisticated argument on the shape of isothermal lines.

The next potential is the free enthalpy  $G(T, p, \mathbf{N})$ , also called Gibbs potential. Just as the free energy it is particularly suitable to grasp systems in contact with a heat bath. But the free enthalpy is particularly useful in situations that in addition allow for an exchange of volume with their environment. We define  $G$  as the Legendre transform of  $U$  with respect to the variable pair  $(S, V)$ , so

$$G(T_B, p_b, \mathbf{N}) = \inf_{S, V} \{U(S, V, \mathbf{N}) - T_B S + p_B V\}. \quad (2.112)$$

The infimum is taken at

$$T_B = \left(\frac{\partial U}{\partial S}\right)_{V, \mathbf{N}} = T \quad (2.113)$$

and

$$p_B = -\left(\frac{\partial U}{\partial V}\right)_{S, \mathbf{N}} = p. \quad (2.114)$$

On using the Gibbs-Duhem equation, one gets

$$G = U - TS + pV = \sum_{i=1}^s \mu_i N_i. \quad (2.115)$$

and

$$dG = -TdS + Vdp + \sum_{i=1}^s \mu_i dN_i. \quad (2.116)$$

Just as the free energy takes the free enthalpy the in the situation it is designed for (both  $T$  and  $p$  being constant) the role of the usable work. Again, we can

take similar steps as above to get an explicit formula for the free enthalpy of the ideal gas. We get, for one species of particles,

$$G(T, p, N) = NT \left( -\frac{f}{2} \ln \frac{T}{T_0} + \ln \frac{p}{p_0} + \left( \frac{f+2}{2} - \frac{S_0}{N_0} \right) \right). \quad (2.117)$$

The last potential, which we only briefly mention, is the great canonical potential  $J(T, V, \mu)$ . It is the Legendre transform of  $(S, N) \mapsto U(S, V, N)$  at fixed  $V$ . As such, it is useful for systems in contact with a heat bath, which in addition can exchange particles with their environment.

## 2.6 Phase transitions

We now come to the final section of our chapter on thermodynamics: On phase transitions. We will hear more about phase transitions later in this course. So let us be brief at this point and merely consider a single example, the one of a phase transition between a fluid and a gas in a van der Waals gas. This is a gas that is not ideal. The equation of state is as follows:

State equation of the van der Waals gas:

$$\left( p + \frac{a}{v^2} \right) (v - b) = cT. \quad (2.118)$$

with constants  $a, b, c > 0$ , where  $v = V/N$ .

At the critical temperature  $T_c$  the two extrema merge and the curve will develop a saddle point, determined by

$$\frac{\partial p}{\partial v} = 0, \quad \frac{\partial^2}{\partial v^2} = 0. \quad (2.119)$$

This condition, applied to Eq. (2.118), gives

$$-\frac{cT}{(v-b)^2} + \frac{2a}{v^3} = 0, \quad (2.120)$$

$$\frac{2cT}{(v-b)^3} - \frac{6a}{v^4} = 0. \quad (2.121)$$

From this, we find the critical temperature

$$cT = \frac{8}{27} \frac{a}{b}. \quad (2.122)$$

The saddle point is at

$$v_c = 3b, \quad p_c = \frac{a}{27b^2}. \quad (2.123)$$

Now, if one now considers the isothermal lines in the  $p$ - $V$ -diagram, one finds “below the critical point” that there is a region where these isotherms are monotone increasing. This contradicts the stability of the system in the form of the convexity of  $F$ . At least in this region the van der Waals equation has to be unphysical. A correction is as follows called the Maxwell construction: This means that  $F$  is replaced by its convex hull.

In effect, this means that a piece of the isothermal is replaced by a horizontal piece for which  $p$  is constant. This is done in a way such that the volume in the  $p$ - $V$ -diagram above and below the constant piece is identical. The free enthalpy is having a kink at the points where the horizontal lines end. It should be clear that now, in this particular case, the state is not completely defined by  $(T, p)$ . The coexistence region proceeds to the critical point, determined above.

The left part corresponds to the gaseous region, to the right one has a fluid. Along the straight lines, both phases are in coexistence. Let us consider the change to the free enthalpy along the straight lines in the  $p$ - $V$ -diagram. Since the particle number of a single species is identical,  $dN = 0$ , we have

$$-S_{\text{fluid}}dT + V_{\text{fluid}}dp = dG = -S_{\text{gas}}dT + V_{\text{gas}}dp. \quad (2.124)$$

Hence, we have for the coexistence line the following equation.

Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{S_{\text{gas}} - S_{\text{fluid}}}{V_{\text{gas}} - V_{\text{fluid}}} = \frac{N}{T} \frac{\delta q}{V_{\text{gas}} - V_{\text{fluid}}}. \quad (2.125)$$

This equation is usually made use of in the case that

$$V_{\text{fluid}} \ll V_{\text{gas}} \approx NT/p. \quad (2.126)$$

Here,  $\delta q$  is the heat quantity that is necessary per particle number that one has to provide to the fluid in order to transform it into a gas.

For real materials, there are usually a number of other phase transitions, often with a number of qualitatively different solid phases. Point where three phases meet are usually called triple points. In particular for systems consisting of a number of different constituents, phase diagrams can look quite complicated.