

# Equilibrium thermodynamics in infinite volume

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## 1 Overview

We will explain the classic thermodynamic formula for the pressure of a gas

$$P = \mu n + T s - \varepsilon , \quad (1)$$

and the related partial derivative identities,

$$\text{chemical potential identity} \quad \left( \frac{\partial \varepsilon}{\partial n} \right)_s = \mu , \quad (2)$$

$$\text{temperature identity} \quad \left( \frac{\partial \varepsilon}{\partial s} \right)_n = T . \quad (3)$$

$$\text{number density identity} \quad \left( \frac{\partial P}{\partial \mu} \right)_T = n , \quad (4)$$

$$\text{entropy density identity} \quad \left( \frac{\partial P}{\partial T} \right)_\mu = s , \quad (5)$$

(6)

From Eqs. (2) and (3), the calculus of partial derivatives gives an additional identity

$$\left( \frac{\partial s}{\partial n} \right)_\varepsilon = - \frac{\left( \frac{\partial s}{\partial \varepsilon} \right)_n}{\left( \frac{\partial n}{\partial \varepsilon} \right)_s} = - \frac{\mu}{T} . \quad (7)$$

## 2 Two independent variables: heat and “charge”

We will look at a typical example of a thermodynamic system, with the following characteristics:

- **Infinite volume limit:** The system is large enough compared to the distance scales of its microscopic physics that we can take the infinite volume limit. This means that the volume of the system is not a relevant variable and everything is expressed in terms of local (intensive) variables.

- **Heat:** The system can store energy in a disordered form that we call *heat*. Heat diffuses from one place to another until it is equally shared by all degrees of freedom (equipartition). The amount of disorder associated with heat is measured by the *entropy*.
- **Conserved “charge”:** There is a conserved quantity, which we call “charge”, whose density is one of the variables that characterizes the state of the system. In many cases, the charge in a given region is just a count of the number of some type(s) of particle, so we will also call it “particle number”. Since we are in the infinite volume limit we don’t use the volume as a state variable. Instead, when we want to talk about compression of the system we phrase it in terms of varying the charge density.
- **Equilibrium:** We assume that the system has settled down into a stable state. That state can be specified by just two numbers: the system has two thermodynamic degrees of freedom, corresponding, perhaps indirectly, to specifying how much heat and how many particles there are per unit volume.

## Examples

A standard example would be a large container of a gas such as nitrogen, with conservation of the number of molecules. This means we restrict ourselves to low enough temperatures and densities so that there are no processes that create or destroy nitrogen molecules.

Another example is beta-equilibrated, electrically neutral nuclear matter, as found in neutron stars. In this case the the conserved charge is baryon number which is not a count of the number of a single type of particle, but is the sum  $N_{\text{neutron}} + N_{\text{proton}}$ . Since there are processes that can convert neutrons to protons and vice versa,  $N_{\text{neutron}}$  and  $N_{\text{proton}}$  are not individually conserved, but their sum is a conserved quantity.

## State variables

There are many parameters we can use to specify the state of the system:

$$\begin{aligned}
 P &\equiv \text{pressure,} \\
 \varepsilon &\equiv \text{energy density,} \\
 \text{Conjugate variables} &\begin{cases} n &\equiv \text{charge (particle number) density,} \\ \mu &\equiv \text{chemical potential for the conserved charge,} \end{cases} \quad (8) \\
 \text{Conjugate variables} &\begin{cases} s &\equiv \text{entropy density,} \\ T &\equiv \text{temperature.} \end{cases}
 \end{aligned}$$

Since the system only has two independent physical properties, corresponding to varying the concentrations of heat and charge, once you specify any two of these variables the rest are then determined. For example, we could treat particle density  $n$  and entropy density  $s$  as the “knobs” that we can vary independently. Then all other quantities,

energy density, pressure, etc, would be functions of them:  $\varepsilon(n, s)$ ,  $P(n, s)$ , etc. Those relationships, which depend on the detailed physics of the system, are called “equations of state”.

### Natural variables $\mu$ and $T$

Two of the state variables are special: the chemical potential  $\mu$  and the temperature  $T$ . They are called “natural variables”. They are special because they are the quantities that become equal when two systems that can freely exchange charge and heat come into equilibrium with each other. If a smaller system is in contact with a large environment, and that environment can feed in or suck out heat and charge, then all we need to know about the environment is its temperature and chemical potential. The smaller system will equilibrate to the state that has the same  $\mu$  and  $T$  as the environment. If the environment and the smaller system have different equations of state then even in equilibrium they may have different values of the other state variables such as  $\varepsilon$ ,  $n$ , or  $s$ , but they must have the same  $\mu$  and  $T$ .

## 3 Pressure

The pressure  $P$  plays a special role because the pressure of a state tells us how physically favored it is. If you fill the two halves of a container with material in two different states, the state with higher pressure will expand, indicating that it is physically favored over the lower pressure state. If you prefer to think in terms of minimizing an energy-like potential rather than maximizing a pressure, you can define the “grand potential”  $\Omega \equiv -P$ , in which case the favored state is the one that minimizes the grand potential.

The standard way of writing the pressure is to think of it as a function of the natural variables, chemical potential and temperature, and write it in the classic form (1),

$$P(\mu, T) = \mu n + T s - \varepsilon . \tag{9}$$

However, it is not clear how to understand this expression. How are the density-type state variables  $\varepsilon$ ,  $n$ , and  $s$  assumed to depend on  $\mu$  and  $T$ ?

### Conjugate pairs

In (1) it is clear that some of the state variables have special relationships: the chemical potential  $\mu$  multiplies the particle density  $n$ , and the temperature  $T$  multiplies the entropy density  $s$ . These “conjugate pairs” (see (8)) can be understood as bias terms that are subtracted from the energy density. One of those terms is  $\mu n$ , so the chemical potential is acting as a bias potential that favors higher particle density. Similarly, temperature acts as a bias potential that favors higher entropy density. Eq. (1) says that the pressure is a double Legendre transform of the energy, where dependence on  $n$  and  $s$  has been transformed into dependence on  $\mu$  and  $T$ .

To understand this properly we will explore two ways of understanding the classic formula (1).

## 4 Parameterizing the states via natural variables $\mu$ and $T$

One way of understanding (1) is to focus on the space of physical states of the system and to parameterize that space by the natural variables, chemical potential  $\mu$  and temperature  $T$ . All the state variables are then functions of  $\mu$  and  $T$ :

$$P(\mu, T) = \mu n(\mu, T) + T s(\mu, T) - \varepsilon(\mu, T) . \quad (10)$$

The dependence of pressure on *two* natural variables,  $\mu$  and  $T$ , captures the fact that we can vary the state of the system in two ways: by adding more particles or by adding more heat.

The problem with this way of approaching (1) is that it obscures the origin of standard thermodynamic identities such as  $n = (\partial P / \partial \mu)_T$  (Eq. (4)). From (10) it is not obvious that this identity is correct, since varying  $\mu$  produces changes in all the state variables  $\varepsilon$ ,  $n$ ,  $s$ . In this approach, you would expect that  $(dP/d\mu)_T$  is just a messy sum of partial derivatives.

## 5 “Extended Pressure” in the larger space of natural and state variables

We can get a deeper understanding of the classic thermodynamic formulae like (1) if we invent a generalization of the pressure which we call “extended pressure”  $\tilde{P}$ . This is function that lives in a larger four-dimensional parameter space where we allow  $\mu$  and  $T$  to vary *independently* of the state variables  $(n, s)$ . The definition of the extended pressure is

$$\text{Extended pressure } \tilde{P}(\mu, T, n, s) \equiv \mu n + T s - \varepsilon(n, s) . \quad (11)$$

Two of the four dimensions come from specifying the state of the system via two of the density-type state variables, in this case  $n$  and  $s$ . The other two dimensions are the natural variables  $\mu$  and  $T$  which we treat as *independent* variables in their own right. In this approach, we think of  $\mu$  and  $T$  as external stimuli or bias potentials.

- In our 4-dimensional parameter space, every point is a valid state of the system in the sense that the density-type state variables  $(\varepsilon, n, s)$  are always related to each other by the equation of state.
- However, for a given state of the system (specified by  $n$  and  $s$ , say) one can have *any* values of the natural variables  $\mu$  and  $T$ . Conversely, for given values of  $\mu$  and  $T$ , we can still explore all possible states of the system by varying  $n$  and  $s$ .
- One might say that the system has “not yet chosen” which state is the most favored for given values of  $\mu$  and  $T$ .

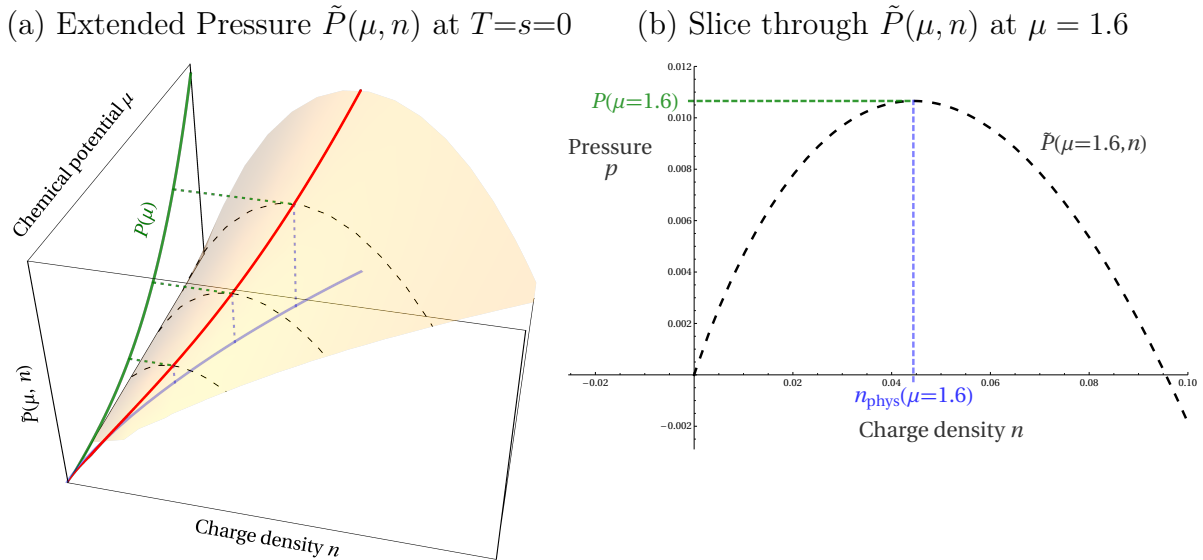


Figure 1: *Left panel:* 3D plot of the extended pressure function  $\tilde{P}(\mu, n)$  for a gas of free nonrelativistic particles at  $T = s = 0$ . The ordinary pressure  $P(\mu)$  (green curve) is the value of the extended pressure  $\tilde{P}(\mu, n)$  on the red line that runs along the top of the ridge. The ridge is defined as the maximum value of  $\tilde{P}(\mu, n)$  when we vary  $n$  at a fixed value of  $\mu$ , e.g., along one of the dashed black lines. *Right panel:* a slice through the 3D plot at a fixed chemical potential, showing how to find the favored state of the system (value of  $n$ ) at a given  $\mu$  by maximizing the extended pressure.

- The 4-dimensional space has a two-dimensional subspace where, for each  $\mu$  and  $T$ , the state variables take their favored values for that  $(\mu, T)$ , meaning the values they would have in a real thermally equilibrated system with that chemical potential and temperature. That is how the ordinary pressure (10) is defined. The favored state is the one that maximizes the pressure.

## 6 Extended pressure: zero temperature case

At zero temperature the entropy density is also zero, so (11) is reduced to

$$\tilde{P}(\mu, n) = \mu n - \varepsilon(n) \quad (12)$$

The situation is illustrated in Fig. 1. The physical states of the system are parameterized by a single variable, the number density  $n$ , and we allow the chemical potential  $\mu$  to vary independently of  $n$ .

In Fig. 1(a) we show the extended pressure function  $\tilde{P}(\mu, n)$  for a gas of free non-relativistic particles, with units chosen so that their mass is  $m = 1$ . At each value of the chemical potential  $\mu$  we can explore all possible states of the system by varying the

number density. In Fig. 1(b) we show one such slice, at  $\mu = 1.6$ . For that value of  $\mu$ , the physically favored state of the system is the one with the highest pressure, so we vary the number density  $n$  to maximize  $\tilde{P}$ . Performing this maximization for every value of  $\mu$ , we trace out a line of maxima, marked by the red line that runs along the top of the ridge in Fig. 1(a).

Projecting downwards into the  $n$ - $\mu$  plane, the blue line traces the positions of the maxima, giving us the relation  $n_{\text{phys}}(\mu)$  that holds for physically favored states,

$$n_{\text{phys}}(\mu) \text{ is defined by } \left( \frac{\partial \tilde{P}}{\partial n} \right)_{\mu}(\mu, n_{\text{phys}}) = 0 \quad (13)$$

Using (12) in (13), we see that

$$\frac{d\varepsilon}{dn}(n_{\text{phys}}) = \mu, \quad (14)$$

which is the zero-temperature version of the chemical potential identity (2).

Projecting sideways, the height of the maximum for each value of  $\mu$  gives us the ordinary pressure function,

$$P(\mu) \equiv \tilde{P}(\mu, n_{\text{phys}}(\mu)). \quad (15)$$

If we want to take the derivative of the pressure along the line of physical states  $n_{\text{phys}}(\mu)$ , all that matters is the explicit  $\mu$  dependence that comes from the  $\mu n$  term; there is no implicit dependence via  $n_{\text{phys}}(\mu)$  because when  $n = n_{\text{phys}}$  the extended pressure is stationary with respect to  $n$ .

$$\begin{aligned} \frac{dP}{d\mu} &= \left( \frac{\partial \tilde{P}}{\partial \mu} \right)_n(\mu, n_{\text{phys}}) + \frac{dn_{\text{phys}}}{d\mu} \underbrace{\left( \frac{\partial \tilde{P}}{\partial n} \right)_{\mu}(\mu, n_{\text{phys}})}_{=0 \text{ from (13)}} \\ &= n_{\text{phys}}(\mu), \end{aligned} \quad (16)$$

which is just the zero-temperature version of the number density identity (4).

## 7 Extended pressure at nonzero temperature

In general, the extended pressure at arbitrary particle and entropy density is (11)

$$\tilde{P}(\mu, T, n, s) = \mu n - Ts - \varepsilon(n, s). \quad (17)$$

Here the charge density and entropy density are independent of the applied potentials  $\mu$  and  $T$ . However, the favored state for given values of  $\mu$  and  $T$  is the one that maximizes the pressure, and this gives us the physical pressure function described in Sec. 4,

$$P(\mu, T) \equiv \tilde{P}(\mu, T, n_{\text{phys}}, s_{\text{phys}}), \quad (18)$$

where  $n_{\text{phys}}$  and  $s_{\text{phys}}$  are determined as functions of  $\mu$  and  $T$  by varying  $n$  and  $s$  until the pressure is maximized,

$n_{\text{phys}}, s_{\text{phys}}$  are the solutions of:

$$\begin{aligned} \left(\frac{\partial \tilde{P}}{\partial n}\right)_{\mu, T, s} (n_{\text{phys}}, s_{\text{phys}}) &= 0, \\ \left(\frac{\partial \tilde{P}}{\partial s}\right)_{\mu, T, n} (n_{\text{phys}}, s_{\text{phys}}) &= 0. \end{aligned} \quad (19)$$

Using (11) we can see how the favored state conditions (19) give us the chemical potential and temperature identities (2) and (3).

### 7.1 Chemical potential and temperature identities

Firstly, as at  $T = 0$ , the particle density of the favored state is whatever maximizes the extended pressure,

$$\text{at } (n, s) = (n_{\text{phys}}, s_{\text{phys}}), \quad \left(\frac{\partial}{\partial n}(\mu n + Ts - \varepsilon(n, s))\right)_{\mu, T, s} = \mu - \left(\frac{\partial \varepsilon}{\partial n}\right)_s = 0, \quad (20)$$

$$\Rightarrow \quad \left(\frac{\partial \varepsilon}{\partial n}\right)_s (n_{\text{phys}}, s_{\text{phys}}) = \mu. \quad (21)$$

This is the ‘‘chemical potential identity’’ (2). Note that it is only valid in the physical subspace where, for a given  $\mu$  and  $T$ , the system is in the physically favored state. Its physical meaning is straightforward: the chemical potential tells us how much energy it costs to add one particle per unit volume (or one unit of the conserved charge) to the system, without adding any heat (hence the derivative is taken at constant entropy density).

Secondly, the entropy density of the favored state is whatever maximizes the extended pressure,

$$\text{at } (n, s) = (n_{\text{phys}}, s_{\text{phys}}), \quad \left(\frac{\partial}{\partial s}(\mu n + Ts - \varepsilon(n, s))\right)_{\mu, T, n} = T - \left(\frac{\partial \varepsilon}{\partial s}\right)_n = 0, \quad (22)$$

$$\Rightarrow \quad \left(\frac{\partial \varepsilon}{\partial s}\right)_n (n_{\text{phys}}, s_{\text{phys}}) = T. \quad (23)$$

This is the ‘‘entropy identity’’ (5). Again, it is only valid in the physical subspace where  $(n, s) = (n_{\text{phys}}(\mu, T), s_{\text{phys}}(\mu, T))$ . It tells us that we can interpret the temperature as the amount of energy it costs to add one unit of entropy to the system without adding any particles (hence the derivative is taken at constant number density).

## 7.2 Number density and entropy density identities

Proceeding in analogy with the zero temperature case (Sec. 6), we can now calculate how the pressure varies along the top of the ridge. This means that as we vary  $\mu$  and  $T$ , we set  $(n, s) = (n_{\text{phys}}(\mu, T), s_{\text{phys}}(\mu, T))$ . Since the physically favored states are stationary points with respect to varying  $n$  and  $s$ , we can ignore the indirect dependence on  $\mu$  and  $T$  that would come via  $n_{\text{phys}}(\mu, T)$  and  $s_{\text{phys}}(\mu, T)$ .

The variation of the pressure with respect to chemical potential is

$$\begin{aligned}
 \left(\frac{\partial P}{\partial \mu}\right)_T &= \left(\frac{\partial \tilde{P}}{\partial \mu}\right)_{T,n,s} + \underbrace{\left(\frac{\partial n_{\text{phys}}}{\partial \mu}\right)_T \left(\frac{\partial \tilde{P}}{\partial n}\right)_{\mu,T,s}(\mu, T, n_{\text{phys}}, s_{\text{phys}})}_{=0 \text{ from (19)}} \\
 &+ \underbrace{\left(\frac{\partial s_{\text{phys}}}{\partial \mu}\right)_T \left(\frac{\partial \tilde{P}}{\partial s}\right)_{\mu,T,n}(\mu, T, n_{\text{phys}}, s_{\text{phys}})}_{=0 \text{ from (19)}} \\
 &= n,
 \end{aligned} \tag{24}$$

which is the number density identity (4).

The variation of the pressure with respect to temperature is

$$\begin{aligned}
 \left(\frac{\partial P}{\partial T}\right)_\mu &= \left(\frac{\partial \tilde{P}}{\partial T}\right)_{\mu,n,s} + \underbrace{\left(\frac{\partial n_{\text{phys}}}{\partial T}\right)_\mu \left(\frac{\partial \tilde{P}}{\partial n}\right)_{\mu,T,s}(\mu, T, n_{\text{phys}}, s_{\text{phys}})}_{=0 \text{ from (19)}} \\
 &+ \underbrace{\left(\frac{\partial s_{\text{phys}}}{\partial T}\right)_\mu \left(\frac{\partial \tilde{P}}{\partial s}\right)_{\mu,T,n}(\mu, T, n_{\text{phys}}, s_{\text{phys}})}_{=0 \text{ from (19)}} \\
 &= s,
 \end{aligned} \tag{25}$$

which is the entropy density identity (5).