

# Appendix A

## The Gibbs-Duhem Relation

### A.1 Homogeneity of the fundamental relation

The Gibbs–Duhem relation follows from the fact that entropy is an extensive quantity and that it is a function of the other extensive variables of the system. An important mathematical result can be derived from *just* this extensivity. We saw that (for a  $pV$  system) entropy is a function of the energy, the volume and the number of particles in the system:  $S = S(E, V, N)$  and this can, formally, be rearranged to write the energy as a function of  $S$ ,  $V$  and  $N$

$$E = E(S, V, N). \quad (\text{A.1.1})$$

This is referred to as the “fundamental relation” for the system.

Now since  $E$ ,  $S$ ,  $V$  and  $N$  are all extensive variables, the fundamental relation function  $E = E(S, V, N)$  is homogeneous. In other words, if the size of the system is multiplied by a constant  $\lambda$  then  $E$ ,  $S$ ,  $V$  and  $N$  are all multiplied by the same  $\lambda$ . Thus

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N). \quad (\text{A.1.2})$$

### A.2 The Euler relation

In order to investigate the consequences of this homogeneity let us differentiate this expression with respect to  $\lambda$ ; we find

$$\begin{aligned} \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \\ \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = E(S, V, N) \end{aligned} \quad (\text{A.2.1})$$

or

$$\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} S + \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} V + \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} N = E(S, V, N) \quad (\text{A.2.2})$$

If we now set the value of  $\lambda$  to unity then the derivatives are simply  $T$ ,  $-p$  and  $\mu$  so that

$$E = TS - pV + \mu N. \quad (\text{A.2.3})$$

Following Callen [1] we shall call this the ‘‘Euler relation’’. This is appropriate because of Euler’s interest in the mathematical properties of homogeneous functions.

### A.3 Two caveats

- We remark, parenthetically, that the student should not be misled by this equation. In learning about thermodynamics one encounters the concept of a function of state, and the fact that heat and work are not functions of state; they depend on path. The Euler relation tells us that there are three contributions to the internal energy:  $TS$ ,  $-pV$  and  $\mu N$ . But we *cannot* identify  $TS$  as the heat content,  $-pV$  as the work content and  $\mu N$  as the chemical content. In other words, the path-dependent  $\int TdS$  is different from the function of state  $TS$ , etc.
- If we had taken  $N$  to be fixed, and thereby ignored  $\mu$  the derivation would not have worked since scaling the system by  $\lambda$  requires that  $N$  be so-scaled. In other words,  $E = TS - pV$  does *not* hold.

### A.4 The Gibbs–Duhem relation

Gibbs–Duhem relation [2] follows from combining the Euler relation with the differential form for  $dE$  (the First Law expression), namely

$$dE = TdS - pdV + \mu dN \quad (\text{A.4.1})$$

to give

$$SdT - Vdp + Nd\mu = 0. \quad (\text{A.4.2})$$

This tells us that the intensive variables  $T$ ,  $p$  and  $\mu$  are *not independent*, which may be surprising. We understand temperature and pressure as (independent) variables over which we have fairly direct control. And by varying

these we can effect heat and volume “flow”. Similarly we learned that particles can be induced to flow by varying the chemical potential. Certainly, our “feel” for chemical potential is not so intuitive as that for temperature and pressure, but we are helped by the mathematical analogies with  $T$  and  $p$ . However, now we see that if we regard  $T$  and  $p$  as independent variables then  $\mu$  depends on  $T$  and  $p$ ; it is not independent.



# Appendix B

## Thermodynamic Potentials

The discussions in this Appendix draw unashamedly on the treatment of Callen[1]. That discussion is so clear and intuitive; it cannot be improved upon. The reader is most certainly advised to read Callen's book at some stage of his/her studies.

### B.1 Equilibrium states

We have seen that the equilibrium state of an isolated system – characterised by  $E, V, N$ , – is determined by maximising the entropy  $S$ . On the other hand we know that a purely mechanical system settles down to the equilibrium state that minimises the energy: the state where the forces  $F_i = -\partial E/\partial X_i$  vanish. In this section we shall see how to relate these two ideas. And then in the following sections we shall see how to extend them.

By a purely mechanical system we mean one with *no* thermal degrees of freedom. This means no changing of the *populations* of the different quantum states – i.e. at constant entropy. But this should also apply for a thermodynamic system at constant entropy. So we should be able to find the equilibrium state in two ways:

- Maximize the entropy at constant energy.
- Minimize the energy at constant entropy.

That these approaches are equivalent may be seen by considering the form of the  $E - S - X$  surface for a system. Here  $X$  is some extensive quantity that will vary when the system approaches equilibrium like the energy in or the number of particles in one half of the system.

At constant energy the plane  $E = E_0$  intersects the  $E - S - X$  surface along a line of possible states of the system. We have seen that the

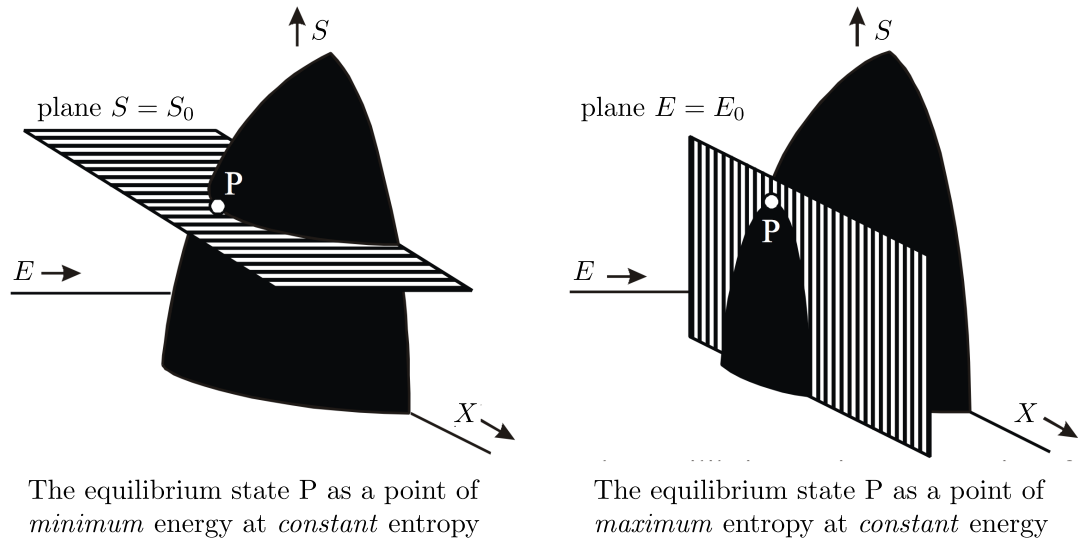


Figure B.1: Alternative specification of equilibrium states (After Callen [1]).

equilibrium state – the state of maximum probability – will be the point of maximum entropy: the point  $P$  on the curve.

But now consider the same system at constant entropy. The plane  $S = S_0$  intersects the  $E - S - X$  surface along a different line of possible states. Comparing the two pictures we see that the equilibrium point  $P$  is now the point of minimum energy.

Equivalence of the entropy maximum and the energy minimum principles depends on the shape of the  $E - S - X$  surface. In particular, it relies on

1.  $S$  having a maximum with respect to  $X$  – guaranteed by the Second Law;
2.  $S$  being an increasing function of  $E$ :  $\partial S / \partial E = 1/T > 0$  means positive temperatures;
3.  $E$  being a single-valued continuous function of  $S$ .

To demonstrate the equivalence of the entropy maximum and the energy minimum principles we shall show that the converse would lead to a violation of the second law.

Assume that the energy  $E$  is *not* the minimum value consistent with a given entropy  $S$ . Then let us take some energy out of the system in the form of work and return it in the form of heat. The energy is then the same but the entropy will have increased. So the original state could not have been an equilibrium state.

The equivalence of the energy minimum and the entropy maximum principle is rather like describing the circle as having the maximum area at fixed circumference or the minimum circumference for a given area.

We shall now look at the specification of equilibrium states when instead of energy or entropy, other variables are held constant.

## B.2 Constant temperature and volume: the Helmholtz potential

To maintain a system of fixed volume at constant temperature we shall put it in contact with a heat reservoir. The equilibrium state can be determined by maximising the total entropy while keeping the total energy constant.

The total entropy is the sum of the system entropy and that of the reservoir. The entropy maximum condition is then

$$\left. \begin{aligned} dS_t &= dS + dS_{\text{res}} = 0 \\ d^2S_t &< 0. \end{aligned} \right\} \quad (\text{B.2.1})$$

The entropy differential for the reservoir is

$$\begin{aligned} dS_{\text{res}} &= \frac{dE_{\text{res}}}{T_{\text{res}}} \\ &= -\frac{dE}{T} \end{aligned} \quad (\text{B.2.2})$$

since the total energy is constant. The total entropy maximum condition is then

$$\left. \begin{aligned} dS - \frac{dE}{T} &= 0 \\ d^2S - \frac{d^2E}{T} &< 0. \end{aligned} \right\} \quad (\text{B.2.3})$$

Or, since  $T$  is constant,

$$\left. \begin{aligned} d(E - TS) &= 0 \\ d^2(E - TS) &< 0, \end{aligned} \right\} \quad (\text{B.2.4})$$

which is the condition for a minimum in  $E - TS$ . But we have encountered  $E - TS$  before, in the consideration of the link between the partition function and thermodynamic properties. This function is the Helmholtz free energy  $F$ . So we conclude that

**at constant  $N$ ,  $V$  and  $T$ ,  $F = E - TS$  is a minimum**  
 — The Helmholtz minimum principle.

We can understand this as a competition between two opposing effects. At high temperatures the entropy tends to a maximum, while at low temperatures the energy tends to a minimum. And the balance between these competing processes is given, at general temperatures, by minimising the combination  $F = E - TS$ .

### B.3 Constant pressure and energy: the Enthalpy function

To maintain a system at constant pressure we shall put it in mechanical contact with a “volume” reservoir. That is, it will be connected by a movable, thermally isolated piston, to a very large volume. As before, we can determine the equilibrium state by maximising the total entropy while keeping the total energy constant. Alternatively and equivalently, we can keep the total entropy constant while minimising the total energy.

The energy minimum condition is

$$\left. \begin{aligned} dE_t = dE + dE_{\text{res}} = 0 \\ d^2E_t > 0. \end{aligned} \right\} \quad (\text{B.3.1})$$

In this case the reservoir may do mechanical work on the system:

$$dE_{\text{res}} = -p_{\text{res}}dV_{\text{res}} = pdV \quad (\text{B.3.2})$$

since the total volume is fixed. We then write the energy minimum condition as

$$\left. \begin{aligned} dE + pdV = 0 \\ d^2E + pd^2V > 0, \end{aligned} \right\} \quad (\text{B.3.3})$$

or, since  $p$  is constant,

$$\left. \begin{aligned} d(E + pV) = 0 \\ d^2(E + pV) < 0. \end{aligned} \right\} \quad (\text{B.3.4})$$

This is the condition for a minimum in  $E + pV$ . This function is called the Enthalpy and it is given the symbol  $H$ . So we conclude that

**at constant  $N$ ,  $p$  and  $E$ ,  $H = E + pV$  is a minimum**  
— The Enthalpy minimum principle.



## B.4 Constant pressure and temperature: the Gibbs free energy

In this case our system can exchange both thermal and mechanical energy with a reservoir; both heat energy and “volume” may be exchanged. Working in terms of the minimum energy at constant entropy condition for the combined system + reservoir:

$$\left. \begin{aligned} dE_t &= dE + dE_{\text{res}} = 0 \\ d^2E_t &> 0. \end{aligned} \right\} \quad (\text{B.4.1})$$

In this case the reservoir exchanges heat energy and/or it may do mechanical work on our system:

$$dE_{\text{res}} = T_{\text{res}}dS_{\text{res}} - p_{\text{res}}dV_{\text{res}} = -TdS + pdV \quad (\text{B.4.2})$$

since the total energy is fixed. We then write the energy minimum condition as

$$\left. \begin{aligned} dE - TdS + pdV &= 0 \\ d^2E - Td^2S + pd^2V &> 0, \end{aligned} \right\} \quad (\text{B.4.3})$$

or, since  $T$  and  $p$  are constant,

$$\left. \begin{aligned} d(E - TS + pV) &= 0 \\ d^2(E - TS + pV) &< 0. \end{aligned} \right\} \quad (\text{B.4.4})$$

This is the condition for a minimum in  $E - TS + pV$ . This function is called the Gibbs free energy and it is given the symbol  $G$ . So we conclude that

**at constant  $N$ ,  $p$  and  $T$ ,  $G = E - TS + pV$  is a minimum**  
 — The Gibbs free energy minimum principle.

## B.5 Differential expressions for the potentials

The internal energy, Helmholtz free energy, enthalpy and Gibbs free energy are called *thermodynamic potentials*. Clearly they are all functions of state. From the definitions

$$\begin{aligned} F &= E - TS && \text{Helmholtz function} \\ H &= E + pV && \text{Enthalph function} \\ G &= E - TS + pV && \text{Gibbs function} \end{aligned} \quad (\text{B.5.1})$$

and the differential expression for the internal energy

$$dE = TdS - pdV \quad (\text{B.5.2})$$

we obtain the differential expressions for the potentials:

$$\begin{aligned} dF &= -SdT - pdV \\ dH &= TdS + Vdp \\ dG &= -SdT + Vdp. \end{aligned} \quad (\text{B.5.3})$$

## B.6 Natural variables and the Maxwell relations

Each of the thermodynamic potentials has its own *natural variables*. For instance, taking  $E$ , the differential expression for the first law is

$$dE = TdS - pdV. \quad (\text{B.6.1})$$

Thus if  $E$  is known as a function of  $S$  and  $V$  then everything else – such as  $T$  and  $p$  – can be obtained by differentiation, since  $T = \partial E / \partial S|_V$  and  $p = -\partial E / \partial V|_S$ . If, instead,  $E$  were known as a function of, say,  $T$  and  $V$ , then we would need more information, such as an equation of state, to completely determine the remaining thermodynamic functions.

All the potentials have their natural variables in terms of which the dependent variables may be found by differentiation:

$$\begin{aligned} E(S, V), \quad dE &= TdS - pdV, \quad T = \left. \frac{\partial E}{\partial S} \right|_V, \quad p = - \left. \frac{\partial E}{\partial V} \right|_S, \\ F(T, V), \quad dF &= -SdT - pdV, \quad S = - \left. \frac{\partial F}{\partial T} \right|_V, \quad p = - \left. \frac{\partial F}{\partial V} \right|_T, \\ H(S, p), \quad dH &= TdS + Vdp, \quad T = \left. \frac{\partial H}{\partial S} \right|_p, \quad V = \left. \frac{\partial H}{\partial p} \right|_S, \\ G(T, P), \quad dG &= -SdT + Vdp, \quad S = - \left. \frac{\partial G}{\partial T} \right|_p, \quad V = \left. \frac{\partial G}{\partial p} \right|_T \end{aligned} \quad (\text{B.6.2})$$

If we differentiate one of these results with respect to a further variable then the order of differentiation is immaterial; differentiation is commutative. Thus, for instance, using the energy natural variables we see that

$$\left. \frac{\partial}{\partial V} \right|_S \left. \frac{\partial}{\partial S} \right|_V = \left. \frac{\partial}{\partial S} \right|_V \left. \frac{\partial}{\partial V} \right|_S \quad (\text{B.6.3})$$

and operating on  $E$  with this we obtain

$$\begin{array}{ccc} \frac{\partial}{\partial V} \Big|_S & \frac{\partial E}{\partial S} \Big|_V & = \frac{\partial}{\partial S} \Big|_V \frac{\partial E}{\partial V} \Big|_S \\ & \parallel & \parallel \\ & T & -p \end{array} \quad (\text{B.6.4})$$

so that we obtain the result

$$\frac{\partial T}{\partial V} \Big|_S = - \frac{\partial p}{\partial S} \Big|_V$$

Similarly, we get one relation for each potential by differentiating it with respect to its two natural variables

$$\begin{array}{l} E : \quad \frac{\partial T}{\partial V} \Big|_S = - \frac{\partial p}{\partial S} \Big|_V \\ F : \quad \frac{\partial S}{\partial V} \Big|_T = \frac{\partial p}{\partial T} \Big|_V \\ H : \quad \frac{\partial T}{\partial p} \Big|_S = \frac{\partial V}{\partial S} \Big|_p \\ G : \quad \frac{\partial S}{\partial p} \Big|_T = - \frac{\partial V}{\partial T} \Big|_p \end{array} \quad (\text{B.6.5})$$

The Maxwell relations give equations between seemingly different quantities. In particular, they often connect easily measured, but uninteresting quantities to difficult-to-measure, but very interesting ones.

Another application of the Maxwell relations is in the study of glassy systems and other quasi-equilibrium states of matter. The validity of the Maxwell relations relies on the assumption of a state of thermal equilibrium. An experimental demonstration that a Maxwell relation does *not* hold is then an indication that the system under investigation is not in a state of thermal equilibrium.



# Appendix C

## Mathematica notebooks

### C.1 Chemical potential of a Fermi gas at low temperatures – Sommerfeld expansion

This approach is based on using the following expression for the Fermi energy in terms of the chemical potential (which must then be inverted)

$$\varepsilon_F^{3/2} = \int_{-\infty}^{\infty} \frac{e^x (kTx + \mu)^{3/2}}{(e^x + 1)^2} dx. \quad (\text{C.1.1})$$

First, specify the order for the power series expansions  $n$ :

**n = 4**

4

Now define the numerator bracket  $zz$

**zz = (kTx + mu)^(3/2)**

(mu + kTx)<sup>3/2</sup>

and then evaluate its power series expansion. We expand this about  $x = 0$ , which is equivalent to expanding about  $\varepsilon = \mu$ .

**sz = Series[zz, {x, 0, n}]**

mu<sup>3/2</sup> +  $\frac{3}{2}k\sqrt{\text{mu}}Tx + \frac{3k^2T^2x^2}{8\sqrt{\text{mu}}} - \frac{(k^3T^3)x^3}{16\text{mu}^{3/2}} + \frac{3k^4T^4x^4}{128\text{mu}^{5/2}} + O[x]^5$

This is a series object. *Mathematica* has convergence problems if we try to integrate it directly. We must convert it to a normal polynomial first. So make it Normal:

**nsz = Normal[sz]**

mu<sup>3/2</sup> +  $\frac{3}{2}k\sqrt{\text{mu}}Tx + \frac{3k^2T^2x^2}{8\sqrt{\text{mu}}} - \frac{k^3T^3x^3}{16\text{mu}^{3/2}} + \frac{3k^4T^4x^4}{128\text{mu}^{5/2}}$

and now we can do the integration. This gives  $\varepsilon_F^{3/2}$ :

**eF32 = Integrate[E^x nsz / (E^x + 1)^2, {x, -Infinity, Infinity}] // Apart**

mu<sup>3/2</sup> +  $\frac{k^2\pi^2T^2}{8\sqrt{\text{mu}}} + \frac{7k^4\pi^4T^4}{640\text{mu}^{5/2}}$

We get  $\varepsilon_F$  by taking the 2/3 power

**eF = eF32^(2/3)**

$$\left(\mu^{3/2} + \frac{k^2\pi^2T^2}{8\sqrt{\mu}} + \frac{7k^4\pi^4T^4}{640\mu^{5/2}}\right)^{2/3}$$

and we express this as a series

**seF = Series[eF, {mu, Infinity, n}]**

$$\mu + \frac{k^2\pi^2T^2}{12\mu} + \frac{k^4\pi^4T^4}{180\mu^3} + O\left[\frac{1}{\mu}\right]^5$$

This is a series for  $\varepsilon_F$  in (inverse) powers of  $\mu$ . We need to revert this series to get  $\mu$  in powers of  $\varepsilon_F$ . But again *Mathematica* behaves strangely, so you need to make it Normal and then expand again as a series:

**neF = Normal[seF]**

$$\mu + \frac{k^2\pi^2T^2}{12\mu} + \frac{k^4\pi^4T^4}{180\mu^3}$$

**sneF = Series[neF, {mu, Infinity, n}]**

$$\mu + \frac{k^2\pi^2T^2}{12\mu} + \frac{k^4\pi^4T^4}{180\mu^3} + O\left[\frac{1}{\mu}\right]^5$$

Now we can revert this series to get  $\mu$  in terms of  $\varepsilon_F$ :

**smu = InverseSeries[sneF, Ef]**

$$Ef - \frac{k^2\pi^2T^2}{12Ef} - \frac{k^4\pi^4T^4}{80Ef^3} + O\left[\frac{1}{Ef}\right]^5$$

and we can make this Normal if necessary

**mmu = Normal[smu]**

$$Ef - \frac{k^2\pi^2T^2}{12Ef} - \frac{k^4\pi^4T^4}{80Ef^3}$$

This is the required low temperature series expression for the chemical potential:

$$\mu = \varepsilon_F \left\{ 1 - \frac{\pi^2}{12} \left(\frac{kT}{\varepsilon_F}\right)^2 - \frac{\pi^4}{80} \left(\frac{kT}{\varepsilon_F}\right)^4 + \dots \right\} \quad (\text{C.1.2})$$

## C.2 Internal energy of a Fermi gas at low temperatures – Sommerfeld expansion

This approach is based on using the following expression for the internal energy in terms of the chemical potential

$$E = \frac{3}{5} \frac{N}{\varepsilon_F^{3/2}} \int_{-\infty}^{\infty} \frac{e^x (kTx + \mu)^{5/2}}{(e^x + 1)^2} dx. \quad (\text{C.2.1})$$

The bracket in the denominator is expanded as a series in powers of temperature and then the integral is evaluated term by term. First, specify the order for the power series expansions  $n$ :

**n = 4**

4

Now define the numerator bracket *zz*

C.2. INTERNAL ENERGY OF A FERMI GAS AT LOW TEMPERATURES – SOMMERFELD EX.

$$\mathbf{zz} = (\mathbf{kTx} + \mathbf{mu})^{5/2}$$

$$(\mathbf{mu} + \mathbf{kTx})^{5/2}$$

and then evaluate its power series expansion. We expand this about  $x = 0$ , which is equivalent to expanding about  $\varepsilon = \mu$ .

$$\mathbf{sz} = \mathbf{Series}[\mathbf{zz}, \{\mathbf{x}, \mathbf{0}, \mathbf{n}\}]$$

$$\mathbf{mu}^{5/2} + \frac{5}{2}\mathbf{kmu}^{3/2}\mathbf{T}x + \frac{15}{8}\mathbf{k}^2\sqrt{\mathbf{mu}}\mathbf{T}^2x^2 + \frac{5\mathbf{k}^3\mathbf{T}^3x^3}{16\sqrt{\mathbf{mu}}} - \frac{5(\mathbf{k}^4\mathbf{T}^4)x^4}{128\mathbf{mu}^{3/2}} + O[x]^5$$

This is a series object. *Mathematica* has convergence problems if we try to integrate it directly. We must convert it to a normal polynomial first. So make it Normal:

$$\mathbf{nsz} = \mathbf{Normal}[\mathbf{sz}]$$

$$\mathbf{mu}^{5/2} + \frac{5}{2}\mathbf{kmu}^{3/2}\mathbf{T}x + \frac{15}{8}\mathbf{k}^2\sqrt{\mathbf{mu}}\mathbf{T}^2x^2 + \frac{5\mathbf{k}^3\mathbf{T}^3x^3}{16\sqrt{\mathbf{mu}}} - \frac{5\mathbf{k}^4\mathbf{T}^4x^4}{128\mathbf{mu}^{3/2}}$$

and now we can do the integration. This gives  $E \varepsilon_F^{3/2} / N$ :

$$\mathbf{enoNoeF32} = (\mathbf{3}/\mathbf{5})\mathbf{Integrate}[\mathbf{E}^{\mathbf{x}}\mathbf{nsz}/(\mathbf{E}^{\mathbf{x}} + \mathbf{1})^{\mathbf{2}}, \{\mathbf{x}, -\mathbf{Infinity}, \mathbf{Infinity}\}]\mathbf{//Apart}$$

$$\frac{3\mathbf{mu}^{5/2}}{5} + \frac{3}{8}\mathbf{k}^2\sqrt{\mathbf{mu}}\pi^2\mathbf{T}^2 - \frac{7\mathbf{k}^4\pi^4\mathbf{T}^4}{640\mathbf{mu}^{3/2}}$$

We need to substitute for  $\mu$ . We get this from a previous calculation (be sure that the order of the series  $n$  is the same).

$$\mathbf{mmu} = \mathbf{Ef} - \frac{\mathbf{k}^2\pi^2\mathbf{T}^2}{12\mathbf{Ef}} - \frac{\mathbf{k}^4\pi^4\mathbf{T}^4}{80\mathbf{Ef}^3} - \frac{247\mathbf{k}^6\pi^6\mathbf{T}^6}{25920\mathbf{Ef}^5} - \frac{16291\mathbf{k}^8\pi^8\mathbf{T}^8}{777600\mathbf{Ef}^7}$$

$$\mathbf{Ef} - \frac{\mathbf{k}^2\pi^2\mathbf{T}^2}{12\mathbf{Ef}} - \frac{\mathbf{k}^4\pi^4\mathbf{T}^4}{80\mathbf{Ef}^3} - \frac{247\mathbf{k}^6\pi^6\mathbf{T}^6}{25920\mathbf{Ef}^5} - \frac{16291\mathbf{k}^8\pi^8\mathbf{T}^8}{777600\mathbf{Ef}^7}$$

We will substitute for  $\mu$  and immediately do a series expansion (to be sure that the expansion is correct to  $n$ th order). This gives the series for  $E \varepsilon_F^{3/2} / N$  as

$$\mathbf{SenoNoeF32} = \mathbf{Series}[(\mathbf{enoNoeF32}/\mathbf{.mu} \rightarrow \mathbf{mmu}), \{\mathbf{T}, \mathbf{0}, \mathbf{n}\}]$$

$$\frac{3\mathbf{Ef}^{5/2}}{5} + \frac{1}{4}\sqrt{\mathbf{Ef}}\mathbf{k}^2\pi^2\mathbf{T}^2 - \frac{3(\mathbf{k}^4\pi^4)\mathbf{T}^4}{80\mathbf{Ef}^{3/2}} + O[\mathbf{T}]^5$$

Now divide by  $\varepsilon_F^{3/2}$  to get  $E/N$ :

$$\mathbf{energyoN} = \mathbf{SenoNoeF32}/\mathbf{Ef}^{(3/2)}\mathbf{//Apart}$$

$$\frac{3\mathbf{Ef}}{5} + \frac{\mathbf{k}^2\pi^2\mathbf{T}^2}{4\mathbf{Ef}} - \frac{3(\mathbf{k}^4\pi^4)\mathbf{T}^4}{80\mathbf{Ef}^3} + O[\mathbf{T}]^5$$

and we can make this Normal if necessary

$$\mathbf{Normal}[\mathbf{energyoN}]$$

$$\frac{3\mathbf{Ef}}{5} + \frac{\mathbf{k}^2\pi^2\mathbf{T}^2}{4\mathbf{Ef}} - \frac{3\mathbf{k}^4\pi^4\mathbf{T}^4}{80\mathbf{Ef}^3}$$

This is the internal energy per particle. So, finally, the internal energy is

$$E = N\varepsilon_F \left\{ \frac{3}{5} + \frac{\pi^2}{4} \left( \frac{kT}{\varepsilon_F} \right)^2 - \frac{3\pi^4}{80} \left( \frac{kT}{\varepsilon_F} \right)^4 + \dots \right\}. \quad (\text{C.2.2})$$





# Appendix D

## Evaluation of the Correlation Function Integral

### D.1 Initial domain of integration

In Section 5.2.1 we made use of the integral identity

$$\int_0^t d\tau_1 \int_0^t d\tau_2 G(\tau_1 - \tau_2) = 2 \int_0^t (t - \tau) G(\tau) d\tau, \quad (\text{D.1.1})$$

which, we stated, was obtained by an appropriate change of variables. In this Appendix we shall show how this result is evaluated.

The integral

$$I = \int_0^t d\tau_1 \int_0^t d\tau_2 G(\tau_1 - \tau_2) \quad (\text{D.1.2})$$

is a two-dimensional integral whose domain of integration is

$$0 < \tau_1 < t, \quad 0 < \tau_2 < t. \quad (\text{D.1.3})$$

In the  $\tau_1 - \tau_2$  plane this is the square with vertices A, B, C, D, shown in Fig. D.1.

### D.2 Transformation of variables

The argument of the integral is  $\tau_1 - \tau_2$ ; this is constant along the lines  $\tau_1 = \tau_2 + \text{const}$ . It thus makes sense to change variables to

$$\begin{aligned} \tau &= \tau_1 - \tau_2 \\ T &= \tau_1 + \tau_2 \end{aligned} \quad (\text{D.2.1})$$

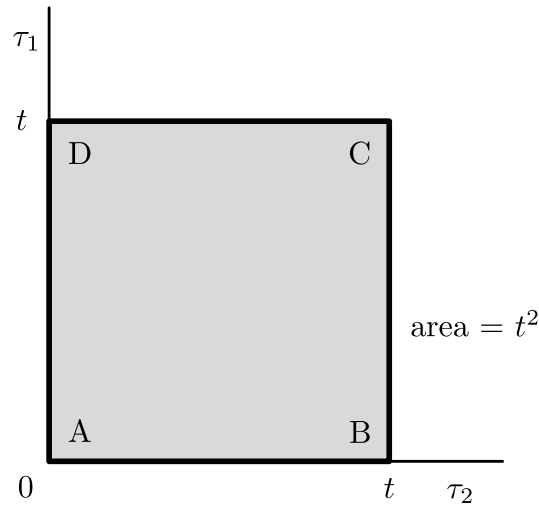


Figure D.1: Original domain of integration

and the domain of integration in terms of the new variables may be found from the location of the vertices:

	$\tau_1$	$\tau_2$	$\tau$	$T$
A	0	0	0	0
B	$t$	0	$t$	$t$
C	$t$	$t$	0	$2t$
D	0	$t$	$-t$	0

Thus the domain of integration in the  $T - \tau$  plane is as shown in Fig. D.2. In terms of the transformed variables the argument of the integral is  $G(\tau)$  and this is independent of the  $T$  variable. So  $G(\tau)$  is constant throughout each slice shown in the figure. Now the slice at height  $\tau$  has width  $2(t - \tau)$  and so its area is  $2(t - \tau)d\tau$ .

### D.3 Jacobian of the transformation

The contribution to the integral from the slice at height  $\tau$  is then  $2(t - \tau)G(\tau)d\tau$ . However, we need to multiply this by the Jacobian  $J$  of the transformation of variables. Thus the integral is

$$I = 2J \int_{-t}^t (t - \tau)G(\tau) d\tau. \quad (\text{D.3.1})$$

The Jacobian is needed since the area of the transformed domain is double that of the original whereas the value of the integral must be independent of

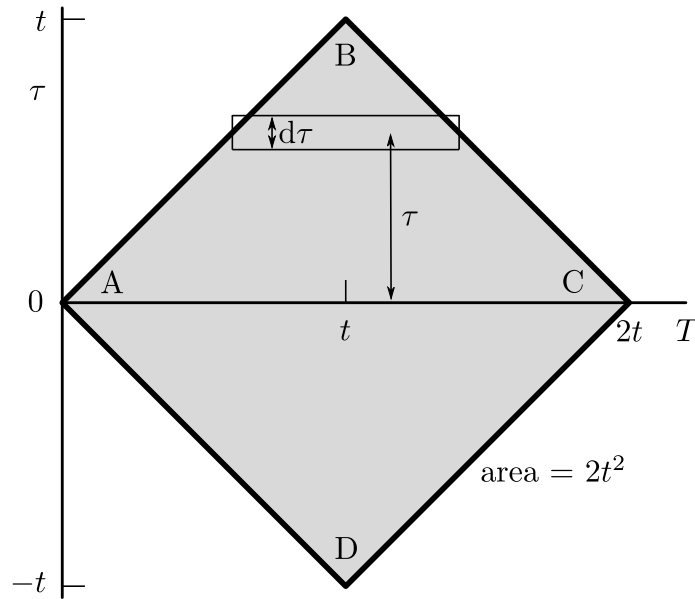


Figure D.2: Transformed domain of integration

the transformation. Consider the case where  $G(\tau) = 1$ . Then

$$I = \int_0^t d\tau_1 \int_0^t d\tau_2 G(\tau_1 - \tau_2) = t^2, \tag{D.3.2}$$

the original domain area. The Jacobian is given by

$$J = \begin{vmatrix} \frac{\partial \tau_1}{\partial \tau} & \frac{\partial \tau_2}{\partial \tau} \\ \frac{\partial \tau_1}{\partial T} & \frac{\partial \tau_2}{\partial T} \end{vmatrix} = \begin{vmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{vmatrix} = \frac{1}{2}, \tag{D.3.3}$$

precisely the required value; this ensures the transformed integral in the case where  $G(\tau) = 1$  has the same value,  $t^2$ . Thus, we conclude that

$$I = \int_{-t}^t (t - \tau) G(\tau) d\tau. \tag{D.3.4}$$

Usually, as indeed we have argued in the previous sections,  $G(\tau)$  is an even function. And in that case we obtain the required result

$$\int_0^t d\tau_1 \int_0^t d\tau_2 G(\tau_1 - \tau_2) = I = 2 \int_0^t (t - \tau) G(\tau) d\tau. \tag{D.3.5}$$



# Appendix E

## Bose-Einstein and Fermi-Dirac Distribution Functions

### E.1 Simple derivation

The derivation of the quantum distribution functions in Chapter 1 was based on the grand canonical approach. Conventional derivations use either the grand canonical or the micro canonical distributions. In many ways the canonical distribution is the most intuitive for many applications, but it is not best-suited to treat the quantum distribution functions. In this section I follow a method based on a discussion in Feynman's book, *Statistical Mechanics* [3]. He used it to obtain the Fermi-Dirac distribution and I have extended it to give the Bose-Einstein distribution also.

We shall find the distribution functions for particles obeying Fermi-Dirac statistics and those obeying Bose-Einstein statistics. Thus we want to know the mean number of particles which may be found in a given quantum state. We start by considering an idealised model, of a subsystem comprising a single quantum state of energy  $\varepsilon$ , in thermal equilibrium with a reservoir of many particles. The mean energy of a particle in the reservoir is denoted by  $\mu$  (we will tighten up on the precise definition of this energy later).

A particle may be in the reservoir or may be in the subsystem. The probability that it is in the subsystem is proportional to the Boltzmann factor  $e^{-\varepsilon/kT}$ , while the probability that it is in the reservoir is proportional to  $e^{-\mu/kT}$ . If  $P(1)$  is the probability that there is one particle in the subsystem and  $P(0)$  is the probability of no particles in the subsystem, then we may write

$$\frac{P(1)}{P(0)} = e^{-(\varepsilon-\mu)/kT} \quad \text{or} \quad P(1) = P(0)e^{-(\varepsilon-\mu)/kT}.$$

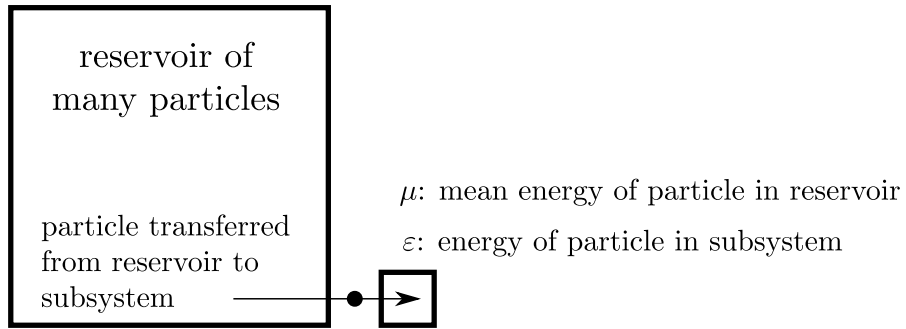


Figure E.1: Transfer of a particle from the reservoir to the subsystem

If the statistics allow (for Bosons, but not for Fermions) then we may transfer more particles from the reservoir to the subsystem. Each particle transferred will lose an energy  $\mu$  and gain an energy  $\varepsilon$ . Associated with the transfer of  $n$  particles there will therefore be a Boltzmann factor of  $e^{-n(\varepsilon-\mu)/kT}$ . And so the probability of having  $n$  particles in the subsystem is

$$P(n) = P(0)e^{-n(\varepsilon-\mu)/kT}. \quad (\text{E.1.1})$$

Let us put

$$x = e^{-(\varepsilon-\mu)/kT}. \quad (\text{E.1.2})$$

Then

$$P(n) = P(0)x^n. \quad (\text{E.1.3})$$

Normalization requires that all possible probabilities sum to unity. For Fermions we know that  $n$  can take on only the values 0 and 1, while for Bosons  $n$  can be any integer. Thus we have

$$\begin{aligned} P(0) + P(1) &= 1 && \text{for Fermions} \\ \sum_{n=0}^{\infty} P(n) &= 1 && \text{for Bosons} \end{aligned}$$

which can be written, quite generally as

$$\sum_{n=0}^a P(n) = 1 \quad (\text{E.1.4})$$

where  $a = 1$  for Fermions and  $a = \infty$  for Bosons.

Since  $P(n)$  is given by Eq. (E.1.3), the normalisation requirement may be expressed as

$$P(0) \sum_{n=0}^a x^n = 1, \quad (\text{E.1.5})$$

which gives us  $P(0)$ :

$$P(0) = \left( \sum_{n=0}^a x^n \right)^{-1}. \quad (\text{E.1.6})$$

We will be encountering the above sum of powers of  $x$  quite frequently, so let's denote it by the symbol  $\Sigma$ :

$$\Sigma = \sum_{n=0}^a x^n. \quad (\text{E.1.7})$$

In terms of this

$$P(0) = \Sigma^{-1} \quad (\text{E.1.8})$$

and then from Eq. (E.1.3)

$$P(n) = x^n / \Sigma. \quad (\text{E.1.9})$$

What we want to know is the *mean* number of particles in the subsystem. That is, we want to calculate

$$\bar{n} = \sum_{n=0}^a nP(n) \quad (\text{E.1.10})$$

which is given by

$$\bar{n} = \frac{1}{\Sigma} \sum_{n=0}^a nx^n. \quad (\text{E.1.11})$$

The sum of  $nx^n$  may be found by using a trick (which is really at the heart of many Statistical Mechanics calculations). The sum differs from the previous sum  $\Sigma$  which we used, because of the extra factor of  $n$ . Now we can bring down an  $n$  from  $x^n$  by differentiation. Thus we write

$$nx^n = x \frac{d}{dx} x^n, \quad (\text{E.1.12})$$

so that

$$\sum_{n=0}^a nx^n = x \frac{d}{dx} \sum_{n=0}^a x^n. \quad (\text{E.1.13})$$

Observe that the sum on the right hand side here is our original sum  $\Sigma$ . This means that  $\bar{n}$  can be expressed as

$$\bar{n} = x \frac{1}{\Sigma} \frac{d\Sigma}{dx} \quad (\text{E.1.14})$$

or

$$\bar{n} = x \frac{d \ln \Sigma}{dx}. \quad (\text{E.1.15})$$

## E.2 Parallel evaluations

It remains, then, to evaluate  $\Sigma$  for the two cases. For Fermions we know that  $a = 1$ , so that the sum in Eq. (E.1.7) is  $1 + x$ . For Bosons  $a$  is infinity; the sum is an infinite (convergent) geometric series. The sum of such a geometric progression is  $1/(1 - x)$ . Thus we have:

<b>Fermions</b>		<b>Bosons</b>
$\Sigma = 1 + x$		$\Sigma = (1 - x)^{-1}$
	the logarithm is:	
$\ln \Sigma = \ln(1 + x)$		$\ln \Sigma = -\ln(1 - x)$
	upon differentiating	
$\frac{d \ln \Sigma}{dx} = \frac{1}{1+x}$		$\frac{d \ln \Sigma}{dx} = \frac{1}{1-x}$
	so that	
$x \frac{d \ln \Sigma}{dx} = \frac{x}{1+x}$		$x \frac{d \ln \Sigma}{dx} = \frac{x}{1-x}$
	and $\bar{n}$ is then given by	
$\bar{n} = \frac{1}{x^{-1}+1}$		$\bar{n} = \frac{1}{x^{-1}-1}$
	Finally, substituting for $x$ from Eq. (E.1.2)	
$\bar{n} = \frac{1}{e^{(\varepsilon-\mu)/kT}+1}$		$\bar{n} = \frac{1}{e^{(\varepsilon-\mu)/kT}-1}$

These expressions will be recognised as the Fermi-Dirac and the Bose-Einstein distribution functions. However, it is necessary to understand the way in which this idealised model relates to realistic assemblies of Bosons or Fermions. We have focussed attention on a given quantum state, and treated it as if it were apart from the reservoir. In reality the reservoir is the entire system and the quantum state of interest is *in* that system. The model analysis then follows through so long as the mean energy of a particle,  $\mu$ , in the system is changed by a negligible amount if a single quantum state is excluded. And this must be so for any macroscopic system.

We now turn to an examination of the meaning of  $\mu$  within the spirit of this picture. We said that it was the mean energy lost when a particle is removed from the reservoir, which we now understand to mean the entire system. When a particle is removed the system remains otherwise unchanged. In particular the distribution of particles in the other energy states is unchanged – the entropy remains constant. Also the energy of the various states is unchanged as the volume remains constant. Thus our  $\mu$  is equal to  $\partial E / \partial N$  at constant  $S$  and  $V$ , which when compared with the extended



statement of the First Law of Thermodynamics:

$$dE = TdS - pdV + \mu dN, \quad (\text{E.2.1})$$

indicates that our  $\mu$  corresponds to the conventional definition of the chemical potential.

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