

# Statistical Physics

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## 5 Applications in thermodynamics

Having worked through statistical mechanics for an ideal gas, we return to investigating issues in thermodynamics.

### 5.1 Maxwell relations

Recalling Fig. 5, we see that we are usually working with two independent thermodynamic variables and two dependent variables. We also have the choice of four potentials with which to work. We rewrite (3.2.8), (3.3.4), (3.3.7), and (3.3.9) here for convenience:

$$\begin{aligned}dE &= TdS - PdV \\dF &= -SdT - PdV \\dG &= -SdT + VdP \\dH &= TdS + VdP.\end{aligned}$$

Often we will want to change which variables we treat as independent. We can derive useful expressions, called **Maxwell relations**, as follows. Assuming  $E(S, V)$  is differentiable then requiring

$$\frac{\partial}{\partial S} \frac{\partial}{\partial V} E(S, V) = \frac{\partial}{\partial V} \frac{\partial}{\partial S} E(S, V) \quad (5.1.1)$$

means that, using (3.2.8),

$$-\left. \frac{\partial P}{\partial S} \right|_V = \left. \frac{\partial T}{\partial V} \right|_S. \quad (5.1.2)$$

Similarly, from

$$\frac{\partial^2}{\partial T \partial V} F(V, T) = \frac{\partial^2}{\partial V \partial T} F(V, T) \quad (5.1.3)$$

and (3.3.4), we find

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V. \quad (5.1.4)$$

Two more relations can be derived from the second derivatives of  $G$  and  $H$ .

Note that these relations are not all independent due to relations between the various first derivatives of  $P$ ,  $S$ ,  $V$ ,  $T$ . Consider a function  $z(x, y)$  (as you did in Part IA Differential Equations). Then

$$dz = \left. \frac{\partial z}{\partial x} \right|_y dx + \left. \frac{\partial z}{\partial y} \right|_x dy. \quad (5.1.5)$$

One can write similar expressions for  $dx$  and  $dy$ , respectively treating  $x$  and  $y$  as the dependent variable. Inserting the expression for  $dx$  into (5.1.5)

$$dz = \left. \frac{\partial z}{\partial x} \right|_y \left[ \left. \frac{\partial x}{\partial y} \right|_z dy + \left. \frac{\partial x}{\partial z} \right|_y dz \right] + \left. \frac{\partial z}{\partial y} \right|_x dy \quad (5.1.6)$$

implies that

$$\left. \frac{\partial z}{\partial x} \right|_y \left. \frac{\partial x}{\partial z} \right|_y = 1 \quad (5.1.7)$$

and

$$\left. \frac{\partial z}{\partial x} \right|_y \left. \frac{\partial x}{\partial y} \right|_z + \left. \frac{\partial z}{\partial y} \right|_x = 0. \quad (5.1.8)$$

A similar substitution for  $dy$  yields

$$\left. \frac{\partial z}{\partial y} \right|_x \left. \frac{\partial y}{\partial x} \right|_z + \left. \frac{\partial z}{\partial x} \right|_y = 0. \quad (5.1.9)$$

Multiplying (5.1.9) by  $(\partial x/\partial z)_y$  yields

$$\left. \frac{\partial z}{\partial y} \right|_x \left. \frac{\partial y}{\partial x} \right|_z \left. \frac{\partial x}{\partial z} \right|_y = -1. \quad (5.1.10)$$

We may also want to change variables so that a function  $f(x, z)$  can be expressed as  $f(x, y)$ . If  $x$  and  $y$  are the independent variables, then

$$df = \left. \frac{\partial f}{\partial x} \right|_y dx + \left. \frac{\partial f}{\partial y} \right|_x dy \quad (5.1.11)$$

and if  $x$  and  $z$  are independent variables

$$df = \left. \frac{\partial f}{\partial x} \right|_z dx + \left. \frac{\partial f}{\partial z} \right|_x dz \quad (5.1.12)$$

$$= \left. \frac{\partial f}{\partial x} \right|_z dx + \left. \frac{\partial f}{\partial z} \right|_x \left[ \left. \frac{\partial z}{\partial x} \right|_y dx + \left. \frac{\partial z}{\partial y} \right|_x dy \right]. \quad (5.1.13)$$

Equating the coefficients of  $dx$  in (5.1.11) and (5.1.13) yields

$$\left. \frac{\partial f}{\partial x} \right|_y = \left. \frac{\partial f}{\partial x} \right|_z + \left. \frac{\partial f}{\partial z} \right|_x \left. \frac{\partial z}{\partial x} \right|_y. \quad (5.1.14)$$

Any of the above relations might be useful in different contexts. The set  $\{x, y, z\}$  may be replaced by any 3 of  $\{P, V, T, S\}$ . For example, if we wish to express  $E(S, V)$  as a function of  $T$  and  $V$  instead, we can use (5.1.14)

$$\begin{aligned} \left. \frac{\partial E}{\partial V} \right|_T &= \left. \frac{\partial E}{\partial V} \right|_S + \left. \frac{\partial E}{\partial S} \right|_V \left. \frac{\partial S}{\partial V} \right|_T \\ &= -P + T \left. \frac{\partial S}{\partial V} \right|_T \\ &= -P + T \left. \frac{\partial P}{\partial T} \right|_V. \end{aligned} \quad (5.1.15)$$

The last step used Maxwell relation (5.1.4). If the equation of state is known, e.g. the ideal gas equation of state  $PV = NkT$ , then we can find  $E(T, V)$ . In the case of the ideal gas, we find

$$\left. \frac{\partial E}{\partial V} \right|_T = -P + T \left( \frac{Nk}{V} \right) = 0 \quad (5.1.16)$$

which implies  $E$  is independent of volume:  $E = E(T)$ . This is consistent with the expression we found last time (4.2.10).

At the risk of revising even more of the mathematical tripos, let us point out how Jacobians can make calculations even shorter (try the example sheet problems with and without Jacobians to compare). In general consider two functions of two variables:  $f(x, y)$  and  $g(x, y)$ . The Jacobian is the determinant given by

$$\frac{\partial(f, g)}{\partial(x, y)} = \begin{vmatrix} \left. \frac{\partial f}{\partial x} \right|_y & \left. \frac{\partial f}{\partial y} \right|_x \\ \left. \frac{\partial g}{\partial x} \right|_y & \left. \frac{\partial g}{\partial y} \right|_x \end{vmatrix} = \left. \frac{\partial f}{\partial x} \right|_y \left. \frac{\partial g}{\partial y} \right|_x - \left. \frac{\partial f}{\partial y} \right|_x \left. \frac{\partial g}{\partial x} \right|_y. \quad (5.1.17)$$

The way we apply these Jacobians is to first write partial derivatives as Jacobians. In the example above, let  $g = y$  so that we can write

$$\frac{\partial(f, y)}{\partial(x, y)} = \left. \frac{\partial f}{\partial y} \right|_y. \quad (5.1.18)$$

In this notation the right-hand side of (5.1.17) reads

$$\frac{\partial(f, g)}{\partial(x, y)} = \frac{\partial(f, y)}{\partial(x, y)} \frac{\partial(g, x)}{\partial(y, x)} - \frac{\partial(f, x)}{\partial(y, x)} \frac{\partial(g, y)}{\partial(x, y)}. \quad (5.1.19)$$

Once we have introduced the Jacobian, we can make quick work of many problems involving change of thermodynamic variables using these properties of Jacobians. Let  $x$  and  $y$  be functions of  $z$  and  $w$  to obtain the chain rule

$$\frac{\partial(f, g)}{\partial(x, y)} = \frac{\partial(f, g)}{\partial(z, w)} \frac{\partial(z, w)}{\partial(x, y)}. \quad (5.1.20)$$

Set  $x = f$  and  $y = g$  to obtain

$$1 = \frac{\partial(x, y)}{\partial(z, w)} \frac{\partial(z, w)}{\partial(x, y)}. \quad (5.1.21)$$

Swap columns or rows to obtain

$$\frac{\partial(f, g)}{\partial(x, y)} = - \frac{\partial(f, g)}{\partial(y, x)} = \frac{\partial(g, f)}{\partial(y, x)}. \quad (5.1.22)$$

These make the relation (5.1.10) verifiable by inspection

$$\frac{\partial(z, x)}{\partial(y, x)} \frac{\partial(y, z)}{\partial(x, z)} \frac{\partial(x, y)}{\partial(z, y)} = -1. \quad (5.1.23)$$

The change of variable relation (5.1.14) follows from the chain rule

$$\begin{aligned}\frac{\partial(f, y)}{\partial(x, y)} &= \frac{\partial(f, y)}{\partial(x, z)} \frac{\partial(x, z)}{\partial(x, y)} \\ &= \left[ \frac{\partial(f, z)}{\partial(x, z)} \frac{\partial(y, x)}{\partial(z, x)} - \frac{\partial(f, x)}{\partial(z, x)} \frac{\partial(y, z)}{\partial(x, z)} \right] \frac{\partial(z, x)}{\partial(y, x)} \\ &= \frac{\partial(f, z)}{\partial(x, z)} + \frac{\partial(f, x)}{\partial(z, x)} \frac{\partial(z, y)}{\partial(x, y)}\end{aligned}\quad (5.1.24)$$

or, taking another choice of arranging the second term

$$\frac{\partial(f, y)}{\partial(x, y)} = \frac{\partial(f, z)}{\partial(x, z)} - \frac{\partial(f, x)}{\partial(y, x)} \frac{\partial(y, z)}{\partial(x, z)}.\quad (5.1.25)$$

As an exercise, prove all the properties of Jacobians above are true, and use them to show

$$\left. \frac{\partial f}{\partial x} \right|_y = - \frac{\left. \frac{\partial f}{\partial y} \right|_x}{\left. \frac{\partial x}{\partial y} \right|_f}.\quad (5.1.26)$$

## 5.2 Heat capacities

Heat is a transfer of energy

$$\mathrm{d}Q = \mathrm{d}E - \mathrm{d}W.\quad (5.2.1)$$

Let us consider systems which change temperature when heat is transferred to or from them. For example we do not consider here systems undergoing a first-order phase transition, like water at its boiling point, where there is a latent heat. In the cases we do consider, we can write

$$\mathrm{d}Q = C \mathrm{d}T\quad (5.2.2)$$

where the quantity  $C$  is called a **heat capacity**. Note that  $1/C$  is an integrating factor for  $\mathrm{d}Q$ , so it must depend on the process. Two useful processes are those done at fixed volume or at fixed pressure. Specialising to reversible processes, for which  $\mathrm{d}Q = T \mathrm{d}S$ , we have heat capacities

$$\boxed{C_V = T \left. \frac{\partial S}{\partial T} \right|_V}\quad (5.2.3)$$

and

$$\boxed{C_P = T \left. \frac{\partial S}{\partial T} \right|_P}.\quad (5.2.4)$$

Recalling  $\mathrm{d}E = T \mathrm{d}S - P \mathrm{d}V$

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V\quad (5.2.5)$$

and recalling  $dH = TdS + VdP$

$$C_P = \left. \frac{\partial H}{\partial T} \right|_P. \quad (5.2.6)$$

Changing variables from  $(T, V)$  to  $(T, P)$

$$T \left. \frac{\partial S}{\partial T} \right|_P = T \left[ \left. \frac{\partial S}{\partial T} \right|_V + \left. \frac{\partial S}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P \right] \quad (5.2.7)$$

or

$$C_P = C_V + T \left. \frac{\partial S}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P \quad (5.2.8)$$

or, applying a Maxwell relation

$$C_P = C_V + T \left. \frac{\partial P}{\partial T} \right|_V \left. \frac{\partial V}{\partial T} \right|_P. \quad (5.2.9)$$

In most systems (I don't know of any exceptions) it is the case that

$$\left. \frac{\partial P}{\partial T} \right|_V > 0 \quad \text{and} \quad \left. \frac{\partial V}{\partial T} \right|_P > 0. \quad (5.2.10)$$

We expect the pressure to go up if we increase the temperature while holding the volume fixed, as in a steam cooker. Likewise, we expect the volume to go up if we increase the temperature while holding the pressure fixed, as in a balloon. Consequently, from (5.2.9)

$$C_P > C_V. \quad (5.2.11)$$

Consider  $dT = dQ|_P/C_P$  compared to  $dT = dQ|_V/C_V$ . Since  $C_P > C_V$ , it requires more heat to raise  $T$  a certain amount if one works at fixed pressure compared to fixed volume. At fixed  $P$ , if  $T$  increases then  $V$  must increase and work is done. Extra heat must be put in since it goes both to raising  $T$  and to raising  $V$ . At fixed  $V$ , no work is done even if  $T$  increases, so all the heat goes into raising  $T$ .

### Example: Ideal gas

Let us take an ideal gas, for example. Furthermore, let us assume that we can use the classical equipartition theorem (we will check this in Chapter 10). For a gas of monatomic particles (no internal degrees-of-freedom) then  $E = (3/2)NkT$  so  $C_V = (3/2)Nk$ . Using (5.2.9) and the equation-of-state (4.2.11) we can find  $C_P = C_V + Nk = (5/2)Nk$ . For atoms in  $D$  dimensions, which have  $d$  internal degrees-of-freedom, then  $E = (N_F/2)NkT$ , where  $N_F = D + d$ . Then  $C_V = (N_F/2)Nk$  and  $C_P = ((N_F/2) + 1)Nk$ . Diatomic molecules, for example, have  $d = 2$  since they can rotate in 2 directions, perpendicular to the axis joining the 2 constituents.

For adiabatic processes  $dQ = 0$ , the first law becomes

$$dE = -P dV. \quad (5.2.12)$$

In general

$$dE = \left. \frac{\partial E}{\partial T} \right|_V dT + \left. \frac{\partial E}{\partial V} \right|_T dV. \quad (5.2.13)$$

The first term is  $C_V dT$  and the second term vanishes for an ideal gas (see (5.1.16)). Combining the previous 2 expressions

$$C_V dT = -P dV \quad (5.2.14)$$

Multiplying both sides by  $Nk$ , and using the equation-of-state (4.2.11) to rewrite  $NkdT$  as  $P dV + V dP$  we find

$$C_V(P dV + V dP) = -Nk P dV. \quad (5.2.15)$$

Grouping like terms and dividing by  $PV$  we find

$$\frac{C_P}{C_V} \frac{dV}{V} = -\frac{dP}{P} \quad (5.2.16)$$

This differential equation is easy enough to solve by integration, arriving at

$$PV^\gamma = \text{constant} \quad (5.2.17)$$

where  $\gamma = C_P/C_V$ , equal to  $5/3$  for a monatomic gas.

### Chemistry notation

There is a slightly different notation in chemistry, where it is more convenient to work with  $n$  **moles** of particles instead of  $N$  particles. Remember **Avogadro's number** is

$$N_A = (6.022 \dots) \times 10^{23} \frac{\text{particles}}{\text{mole}} \quad (5.2.18)$$

and one defines an ideal gas constant

$$R = N_A k \quad (5.2.19)$$

so that  $Nk = nR$ . Then one can define **specific heats**  $c_V = C_V/n$  and  $c_P = C_P/n$ , the heat capacities per mole.

## 5.3 Carnot cycle

Using the ideas presented so far, Carnot gave a simple, illustrative model for an engine which converts heat into work. Consider an ideal gas in a container, with one end comprised of a movable piston. We put the system through repeated cycles of 4 steps (see Fig. 8). In the first step, the container is connected to a heat source and both the source and the system are at temperature  $T_1$ . The piston is pulled up, allowing the gas to expand, but in a way such that the temperature stays fixed at  $T_1$ . This is an **isothermal** step. At some point the heat source is removed and the expansion switches to an adiabatic expansion, with  $Q = 0$ . The expansion stops when the gas cools to a temperature  $T_3$ , at which point a heat sink, also at

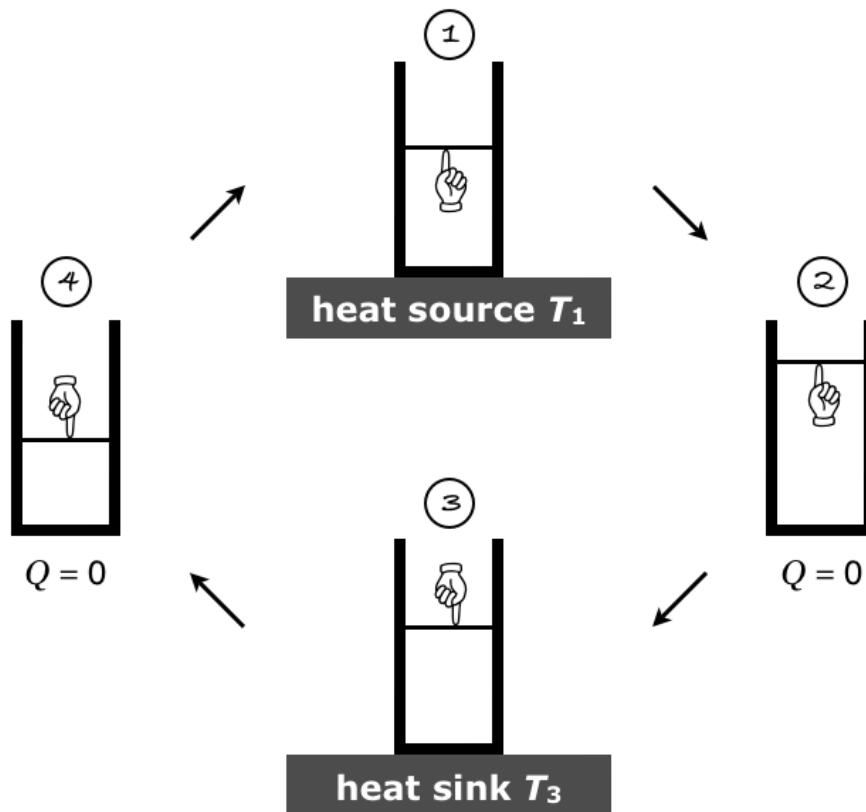


Figure 8: The four steps of the Carnot cycle. (See text for description.)

temperature  $T_3$ , is introduced. At this stage the gas is then isothermally compressed until it reaches some point, at which the heat sink is removed. The compression continues adiabatically until the gas heats back up to  $T_1$ . The cycle is repeated at will.

The 2 graphs in Fig. 9 show the behaviour of the state variables. The behaviour of  $T$  and  $S$  is simple at each stage: temperature is constant during the isothermal steps, and entropy is constant during the adiabatic steps ( $\delta Q = TdS$ ). The behaviour of  $P$  and  $V$  can be determined straightforwardly. During isothermal stages 1 and 3, pressure and volume have to multiply to equal a constant according to the equation of state. During adiabatic stages 2 and 4 we know  $PV^\gamma$  remains constant. Thus

$$\begin{aligned} \text{along 1:} \quad PV &= NkT_1 \\ \text{along 2:} \quad PV^\gamma &= K_2 \\ \text{along 3:} \quad PV &= NkT_3 \\ \text{along 4:} \quad PV^\gamma &= K_4. \end{aligned}$$

Ideally, with no friction or loss,  $\Delta S = 0$  during one complete cycle. As we said, the entropy is unchanged during adiabatic expansion or compression:  $(\Delta S)_2 = 0 = (\Delta S)_4$ . During the isothermal expansion  $(\Delta S)_1 = Q_1/T_1$  and during the isothermal compression  $(\Delta S)_3 = Q_3/T_3$ , where  $Q_1 > 0$  and  $Q_3 < 0$  are the amounts of heat transferred to the system. The requirement that the system returns to its initial



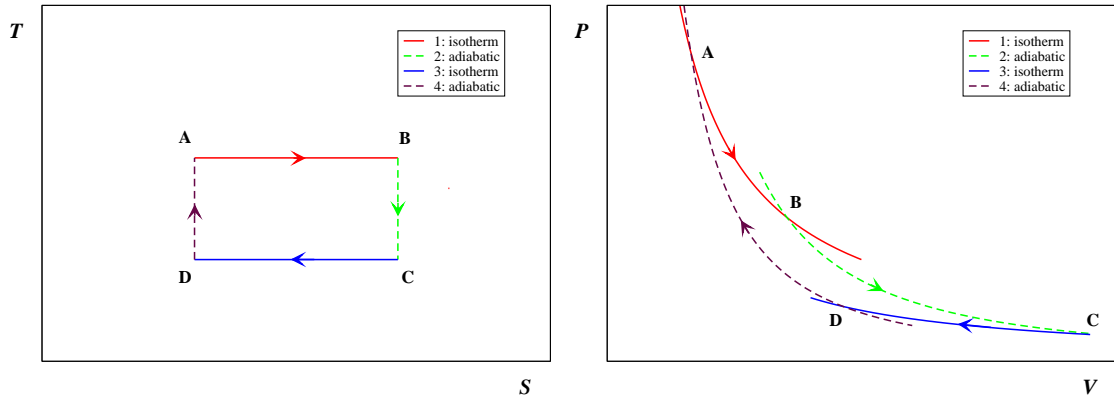


Figure 9: (Colour online) Path followed during the Carnot cycle in the  $(S, T)$  plane (left) and the  $(V, P)$  plane (right).

state after one complete cycle means that

$$\Delta S = \frac{Q_1}{T_1} + 0 + \frac{Q_3}{T_3} + 0 = 0. \quad (5.3.1)$$

Therefore

$$|Q_3| = T_3 \frac{|Q_1|}{T_1}. \quad (5.3.2)$$

Given that  $T_3 < T_1$ , we see that the heat extracted from the system  $-Q_3$  is less than the heat delivered to the system  $Q_1$ . That heat is converted to work, as we will see shortly.

If the system is not ideal then heat is lost through inefficiency. The engine itself is not a closed system. In order to apply the second law of thermodynamics we need to consider the engine and its environment. The environment has heat  $-Q_1$  taken away from it by the engine in stage 1, and heat  $-Q_3$  is returned back to the environment in stage 3. While the engine returns to its initial state after one cycle, the environment does not if there are any inefficiencies (*i.e.* if it is a realistic engine). For the environment

$$\Delta S = -\frac{Q_1}{T_1} - \frac{Q_3}{T_3} \geq 0. \quad (5.3.3)$$

Thus any inefficiency implies

$$|Q_3| > T_3 \frac{|Q_1|}{T_1}. \quad (5.3.4)$$

In words, there is a minimum amount of heat that is returned to the environment for any  $T_3 > 0$ . It is impossible to construct a perfect engine which converts all delivered heat into work. One defines the **efficiency** of a Carnot engine to be

$$\eta = \frac{|Q_1| - |Q_3|}{|Q_1|} = \frac{T_1 - T_3}{T_1}. \quad (5.3.5)$$

We can actually calculate the work done on the system (which we should expect to be negative for an engine – it's the one designed to be doing the work!) We

already saw that  $dW = -P dV$  (3.1.1) and  $dW = dE - dQ$  (3.2.9). Integrating over the full cycle (see right graph in Fig. 9) we get 4 contributions to the net work done on the system:

$$W_1 = -NkT_1 \int_A^B \frac{dV}{V} = -NkT_1 \left( \log \frac{V_B}{V_A} \right) \quad (5.3.6)$$

$$W_2 = \int_B^C dE = -C_V(T_1 - T_3) \quad (5.3.7)$$

$$W_3 = -NkT_3 \int_C^D \frac{dV}{V} = NkT_3 \left( \log \frac{V_C}{V_D} \right) \quad (5.3.8)$$

$$W_4 = \int_D^A dE = C_V(T_1 - T_3) \quad (5.3.9)$$

The quantities on the right-hand sides are written so that the terms in parentheses are positive. So we see that positive work is done *by* the system in stages 1 and 2, and positive work is done *on* the system in stages 3 and 4. The area under curves 1 + 2 is greater than the area under curves 3 + 4, so we confirm that the engine does net work over a complete cycle.

Note that along the adiabatics, we can combine  $PV^\gamma = \text{constant}$  with  $PV = NkT$  to find

$$TV^{\gamma-1} = \text{constant}. \quad (5.3.10)$$

Applying this to curves 2 and 4, we have

$$\begin{aligned} T_1 V_B^{\gamma-1} &= T_3 V_C^{\gamma-1} \\ T_3 V_D^{\gamma-1} &= T_1 V_A^{\gamma-1} \end{aligned}$$

which imply

$$\frac{V_C}{V_D} = \frac{V_B}{V_A}. \quad (5.3.11)$$

Adding together all these contributions the net work done *on* the system is

$$W = -Nk(T_1 - T_3) \log \frac{V_B}{V_A}. \quad (5.3.12)$$

## 5.4 Model of a non-ideal gas

We briefly deviate from our main example, the ideal gas, to discuss a simple model of realistic gases. The van der Waals model modifies the ideal gas law to include a finite radius for the particles and a parameter accounting for weak attractive interactions. A useful potential which includes these effects is the Lennard-Jones potential (Fig. 10)

$$U(r) = A \left( \frac{r_0}{r} \right)^{12} - B \left( \frac{r_0}{r} \right)^6 \quad (5.4.1)$$

where  $r_0$  is the length scale at which the potential switches from hard-core repulsion to weak attraction;  $A$  and  $B$  are constants.

To account for the finite size of constituents in the van der Waals model, we say that each particle occupies volume  $b$ . Then the effective volume  $V_{\text{eff}}$  we should insert

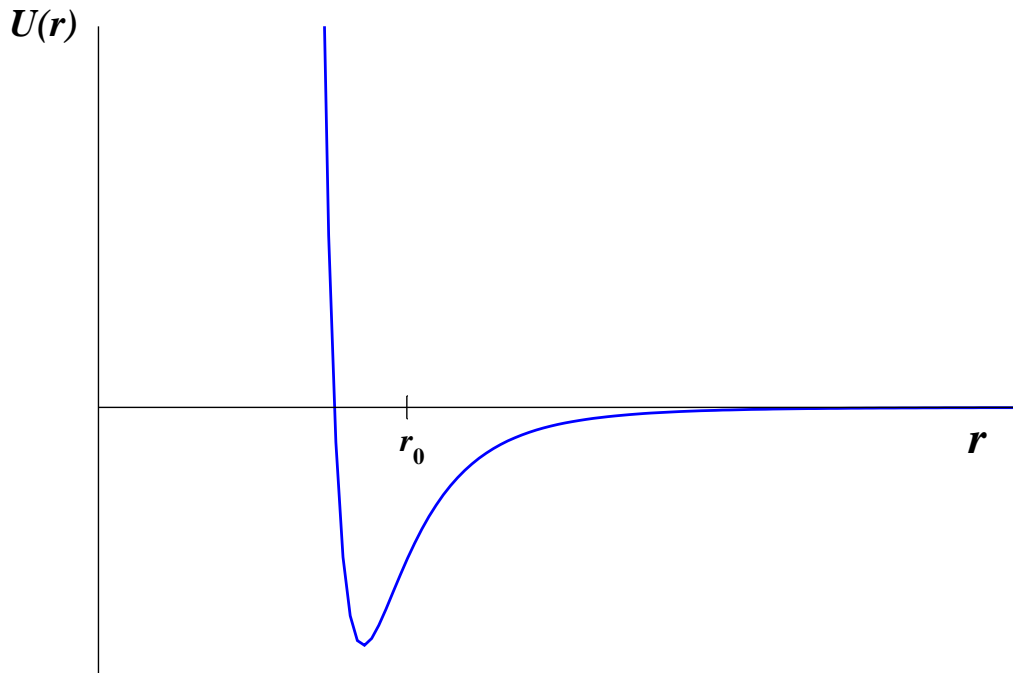


Figure 10: Lennard-Jones potential, an empirical potential describing van der Waals interactions between atoms or molecules.

in the equation-of-state is the difference of the container's volume  $V$  and the space taken up by the particles

$$V_{\text{eff}} = V - bN. \quad (5.4.2)$$

In the presence of weak attraction, the particles at the boundary of the container will feel a net attraction toward the centre of the system, consequently exerting less pressure on the container walls. The number of pairs interacting near the wall of area  $\mathcal{A}$  is  $(N/V)^2 \mathcal{A}$ . Thus the difference between the pressure we would measure if interactions were absent and the realistic pressure is

$$P_{\text{eff}} - P_{\text{meas}} = a \left( \frac{N}{V} \right)^2. \quad (5.4.3)$$

It is  $P_{\text{eff}}$  rather than the measured pressure which should appear in the modified ideal gas equation-of-state. Therefore we arrive at the **van der Waals equation**

$$\boxed{\left( P + \frac{aN^2}{V^2} \right) (V - bN) = NkT.} \quad (5.4.4)$$

where we dropped the subscript from  $P_{\text{meas}}$ .

### Further reading

1. F Mandl, *Statistical Physics*, (Wiley & Sons, 1988), Chapter 5.

2. F Reif, *Fundamentals of Thermal and Statistical Physics*, (McGraw-Hill, 1965), §§10.3-10.5.
3. M Planck, *Treatise on Thermodynamics*, (Dover, 1945), Chapters II.i and II.ii.