1 Elements of Thermodynamics

This first chapter is devoted to a quick review of some key facts of thermodynamics. We begin with the laws of thermodynamics, before turning to thermodynamic potentials and the Maxwell relations. We conclude with a discussion of stability criteria for thermodynamic systems.

1.1 The Laws of Thermodynamics

Let us begin with a brief recollection of the principles of thermodynamics. Our starting point are the first two laws.

First Law: A thermodynamic system can perform work W at the expense of a variation of internal energy ΔU and a heat exchange Q with the environment, and the three quantities are related according to

$$\Delta U = Q - W. \tag{1.1}$$

Note that, while ΔU depends only on the initial and final states, the two other terms depend on the specific transformation. Infinitesimally, this translates to

$$dU = \delta Q - \delta W, \tag{1.2}$$

where dU is an exact differential, while δQ and δW are not. For most systems of interest in the following chapters,

$$\delta W = P \, dV, \tag{1.3}$$

where P is their pressure and V is their volume.

Second Law: For any cyclic transformation,

$$\oint \frac{\delta Q}{T} \leq 0, \tag{1.4}$$

where T is the temperature of the external source. This is also known as Clausius inequality. The inequality is saturated for *reversible* transformations, that is those in which the system proceeds through equilibrium configurations.
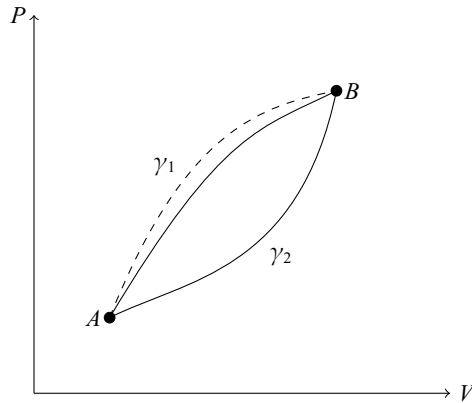
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A schematic illustration of γ_1 and γ_2 in the *PV* plane. The transformation γ_1 can be reversible, in which case the system goes through equilibrium configurations (solid line), or irreversible (dashed line).

By considering a cycle comprising a transformation $\gamma_1(A, B)$ from a state A to a state B and a *reversible* transformation $\gamma_2(B, A)$ from B to A as in Figure 1.1, one can conclude that

$$\int_{\gamma_1(A,B)} \frac{\delta Q}{T} + \int_{\gamma_2(B,A)} \frac{\delta Q_{\text{rev}}}{T} \leq 0. \tag{1.5}$$

Since γ_2 is reversible, one can also recast this relation in the form

$$\int_{\gamma_1(A,B)} \frac{\delta Q}{T} \leq \int_{\gamma_2(A,B)} \frac{\delta Q_{\text{rev}}}{T} = \Delta S(A, B), \tag{1.6}$$

where we have also defined the entropy difference $\Delta S(A, B)$ between state A and state B.

This result has a few noteworthy consequences. To begin with, choosing γ_1 to be reversible, one can conclude that $\Delta S(A, B)$ is independent of the choice of reversible path between A and B. Moreover, if the system is isolated during γ_1,

$$\Delta S \geq 0 \tag{1.7}$$

because $\delta Q = 0$. Finally, if A and B are infinitesimally separated,

$$T\, dS \geq \delta Q. \tag{1.8}$$

We have defined the entropy up to an additive constant, which could be associated to an arbitrary reference state. However, we can anticipate that in statistical physics the additive constant is naturally fixed via Boltzmann's formula, which we shall meet in Eq. (2.16),

$$S = k_B \log \Gamma, \tag{1.9}$$

where $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. This expression links the entropy of a given thermodynamic state to the number, Γ, of microscopic configurations (microstates) that correspond to it. In this fashion, one is setting to zero the entropy of the "ordered" thermodynamic states that correspond to a single microstate.

While we shall return to this issue in Chapter 2, one can argue that Boltzmann's formula follows from the requirement that S, like U or Q, be an *extensive* quantity.[1] Indeed, a pair of independent sub-systems with Γ_1 and Γ_2 microstates build a system with $\Gamma = \Gamma_1 \Gamma_2$ microstates. Letting $S = f(\Gamma)$, and demanding that it be the sum of two entropies S_1 and S_2 of the sub-systems, the function f should satisfy

$$f(\Gamma_1\Gamma_2) = f(\Gamma_1) + f(\Gamma_2), \tag{1.10}$$

and one can show that Eq. (1.9), with a constant k, is the only continuous solution of this functional equation.

> **Third Law:** In the $T \to 0$ limit, thermodynamic systems approach orderly states, and the entropy should have a *nonsingular* behavior, independent of pressure or volume.

This limit can be well defined only if Nernst's theorem,

$$\lim_{T\to 0} C_V(T) = 0, \tag{1.11}$$

holds, where

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{1.12}$$

is the specific heat at constant volume. We shall see that quantum mechanics is instrumental to this effect. A nonzero limit for C_V would indeed imply, for a reversible transformation performed at fixed volume, a logarithmically divergent

$$\Delta S = \int_{\gamma(A,B)} C_V(T) \, \frac{dT}{T} \tag{1.13}$$

as the state A approaches $T = 0$.

1.2 Thermodynamic Potentials

We can now recall a number of facts concerning thermodynamic potentials, while confining our attention to reversible transformations. The various thermodynamic potentials are characterized by different groups of natural variables. While the entropy remains constant in reversible transformations of isolated systems, the other potentials that we recall here, the enthalpy and the Helmholtz, Gibbs, and Grand potentials, remain constant when different groups of control variables are held fixed.

Let us begin from the *internal energy U*, for which the first and second laws imply the differential form

$$dU = T \, dS - P \, dV + \mu \, dN, \tag{1.14}$$

where we have also introduced the *chemical potential* μ, a possibly less familiar thermodynamic function that is not *extensive* like V, U, A, or G, but is *intensive* like

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[1] Extensive quantities grow proportionally to the size of the system, while intensive ones are independent of it.

T and P. As we shall see, it characterizes diffusive equilibria. This expression also manifests the natural variables for U, which are S, V, and N, and the corresponding derivatives,

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}, \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}, \tag{1.15}$$

therefore have a universal meaning. Moreover, demanding that mixed derivatives coincide leads to the *Maxwell relations*

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}, \quad \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N},$$

$$\left(\frac{\partial P}{\partial N}\right)_{S,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{S,N}. \tag{1.16}$$

The specific heat at constant volume C_V, which we first introduced in Eq. (1.12), can be related to U and S according to

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N}. \tag{1.17}$$

Alternatively, one can invert Eq. (1.14) to regard the *entropy* as a thermodynamic potential with natural variables U, V, and N, so that

$$dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN, \tag{1.18}$$

and therefore

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}, \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}. \tag{1.19}$$

One can now define the *enthalpy*,

$$H = U + PV, \tag{1.20}$$

and Eq. (1.14) implies that

$$dH = TdS + VdP + \mu dN, \tag{1.21}$$

so that

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}, \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N}, \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}. \tag{1.22}$$

The equality of mixed derivatives now implies the additional Maxwell relations

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

$$\left(\frac{\partial V}{\partial N}\right)_{S,P} = \left(\frac{\partial \mu}{\partial P}\right)_{S,N}. \tag{1.23}$$

One is also led to define the specific heat at constant pressure C_P, according to

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N}. \tag{1.24}$$

The *Helmholtz free energy* is then defined as

$$A = U - TS, \tag{1.25}$$

and Eq. (1.14) implies that

$$dA = -S\,dT - P\,dV + \mu\,dN, \tag{1.26}$$

so that

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}. \tag{1.27}$$

The equality of mixed derivatives now implies the additional Maxwell relations

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}, \quad \left(\frac{\partial S}{\partial N}\right)_{T,V} = -\left(\frac{\partial \mu}{\partial T}\right)_{V,N},$$

$$\left(\frac{\partial P}{\partial N}\right)_{T,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,N}. \tag{1.28}$$

The *Gibbs free energy* is defined as

$$G = A + PV, \tag{1.29}$$

and therefore

$$dG = -S\,dT + V\,dP + \mu\,dN, \tag{1.30}$$

so that

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}. \tag{1.31}$$

The equality of mixed derivatives now implies one more set of Maxwell relations:

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}, \quad \left(\frac{\partial S}{\partial N}\right)_{T,P} = -\left(\frac{\partial \mu}{\partial T}\right)_{P,N},$$

$$\left(\frac{\partial V}{\partial N}\right)_{T,P} = \left(\frac{\partial \mu}{\partial P}\right)_{T,N}. \tag{1.32}$$

There is something interesting here: insofar as G is an extensive function, it should scale proportionally to the number N of particles, but it is naturally a function of N and of the two intensive variables T and P. As a result

$$G(T,P,N) = N\mu(T,P), \tag{1.33}$$

so that G and the chemical potential μ are intimately related, and consequently

$$d\mu = -s\,dT + v\,dP, \tag{1.34}$$

with

$$s = \frac{S}{N}, \qquad v = \frac{V}{N} \tag{1.35}$$

describing the specific entropy and the specific volume, or the entropy and volume per particle.

Finally, the *Grand Potential* is defined as

$$\Omega = A - \mu N, \tag{1.36}$$

and therefore

$$d\Omega = -S\,dT - P\,dV - N\,d\mu, \tag{1.37}$$

so that

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}, \quad P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}, \quad N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}. \tag{1.38}$$

The equality of mixed derivatives now implies a final set of Maxwell relations

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

$$\left(\frac{\partial P}{\partial\mu}\right)_{T,V} = \left(\frac{\partial N}{\partial V}\right)_{T,\mu}. \tag{1.39}$$

Again, insofar as Ω is an extensive function, which should depend on V and on the two intensive variables T and μ,

$$\Omega(T,V,\mu) = -P(T,\mu)\,V, \tag{1.40}$$

on account of Eq. (1.37).

Note that an additional step to build $\Omega + PV$ would apparently lead to a thermodynamic potential depending only on the intensive variables (T,P,μ), which can only vanish by consistency. In this fashion one can recover Eqs. (1.33) and (1.34).

1.3 Comparison between C_P and C_V

We can now explore some important consequences of thermodynamics, and to begin with we would like to compare the two types of specific heats that we have encountered in Eqs. (1.17) and (1.24). There is a nice trick to do this, which is used at length in the classic text of Landau and Lifshitz. It rests on an important property of Jacobians, which satisfy the chain rule like ordinary derivatives. Jacobians associated to 2×2 matrices of the type

$$\frac{\partial(A,B)}{\partial(C,D)} = \det \begin{vmatrix} \left(\frac{\partial A}{\partial C}\right)_D & \left(\frac{\partial A}{\partial D}\right)_C \\ \left(\frac{\partial B}{\partial C}\right)_D & \left(\frac{\partial B}{\partial D}\right)_C \end{vmatrix} \tag{1.41}$$

can be used to express C_V as

$$C_V = T\frac{\partial(S,V)}{\partial(T,V)} = T\frac{\partial(S,V)}{\partial(T,P)}\frac{\partial(T,P)}{\partial(T,V)} = T\frac{\partial(S,V)}{\partial(T,P)}\left(\frac{\partial P}{\partial V}\right)_T. \tag{1.42}$$

Expanding the remaining determinant gives

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P, \tag{1.43}$$

and the first term is C_P, so that one can conclude that

$$C_V = C_P + T\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2\left(\frac{\partial P}{\partial V}\right)_T, \tag{1.44}$$

where we have used

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = 1 \tag{1.45}$$

and a Maxwell relation in Eq. (1.32). We shall prove shortly that, in general,

$$\left(\frac{\partial P}{\partial V}\right)_T \leq 0, \tag{1.46}$$

so that, under the same circumstances, $C_P \geq C_V$, and for a stable equilibrium, as we are about to see, the strong inequality $C_P > C_V$ holds. In Chapter 6 we shall elaborate on some subtleties that emerge in the presence of first-order phase transitions.

1.4 Fluctuations

We can now discuss three types of equilibrium conditions for a pair of subsystems, and their important implications.

1. **Thermal Equilibrium**

   Let us consider two subsystems $\mathcal{S}_1$ and $\mathcal{S}_2$ of a given isolated system $\mathcal{S}$ of fixed volumes, in *thermal contact* with each other and weakly interacting, so that for the entropy one can conclude that $S \simeq S_1 + S_2$. If the energy of subsystem $\mathcal{S}_1$ undergoes a variation dU_1, the energy of subsystem $\mathcal{S}_2$ thus undergoes the opposite variation $dU_2 = -dU_1$. Consequently, the total entropy change is

$$dS = \left(\frac{\partial S_1}{\partial U}\right)_V dU_1 + \left(\frac{\partial S_2}{\partial U}\right)_V dU_2 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1. \tag{1.47}$$

   We know from the second law of thermodynamics that for an isolated system $dS \geq 0$, and therefore if $dU_1 > 0$ one can conclude that $T_1 < T_2$, and vice versa. In other words, heat flows from warmer bodies to colder ones. If the two systems are in thermal equilibrium, S does not vary and the two temperatures T_1 and T_2 coincide. This fact is often referred to as the *zeroth law of Thermodynamics*.

2. **Mechanical Equilibrium**

   Let us again consider two subsystems $\mathcal{S}_1$ and $\mathcal{S}_2$, in *thermal* equilibrium and thus at the same temperature T, but in *mechanical contact* with each other via a moving partition and again weakly interacting, so that $S \simeq S_1 + S_2$. Hence, if the volume of subsystem $\mathcal{S}_1$ undergoes a variation dV_1, the volume of subsystem $\mathcal{S}_2$ undergoes the opposite variation $dV_2 = -dV_1$. The total entropy change is thus

$$dS = \left(\frac{\partial S_1}{\partial V}\right)_T dV_1 + \left(\frac{\partial S_2}{\partial V}\right)_T dV_2 = \frac{1}{T} (P_1 - P_2) dV_1. \tag{1.48}$$

   We know from the second law of thermodynamics that for an isolated system $dS \geq 0$, and therefore if $dV_1 > 0$ one can conclude that $P_1 > P_2$, and vice versa. In other words, we have recovered another well-known fact: the partition moves toward the region with lower pressure. In equilibrium, the two pressures P_1 and P_2 coincide.

3. **Diffusive Equilibrium**

Consider now two systems in equilibrium that can exchange particles, and consider variations dN_1 and dN_2, in the same spirit of what we did above, for a pair of systems in *thermal* and *mechanical* equilibrium, and thus at the same temperature T and at the same pressure P. This leads to

$$dS = \left(-\mu_1 + \mu_2\right) \frac{dN_1}{T}, \tag{1.49}$$

so that demanding that $dS \geq 0$ one can deduce that $\mu_1 \geq \mu_2$ if $dN_1 < 0$, and vice versa. In other words, the particles tend to move into the system with lower chemical potential, and in equilibrium the two chemical potentials μ_1 and μ_2 coincide.

1.5 Stability

We can now turn to fluctuations, and to this end let us consider a subsystem 1 of a large system 2, which should be in thermal and mechanical equilibrium within it, thus having the same temperature T_0 and the same pressure P_0 as the larger system, according the first and second equilibrium conditions given in Section 1.4. Our task is to compute the variation of the internal energy U, which depends naturally on the thermodynamic variables that are not fixed a priori, S and V. Keeping terms up to second order while leaving implicit, for brevity, the variables that are kept fixed, the result is

$$dU_1 = T_0 \, dS_1 - P_0 \, dV_1 \tag{1.50}$$
$$+ \frac{1}{2} \left[\frac{\partial^2 U_1}{\partial S^2} \, dS_1^2 + 2 \frac{\partial^2 U_1}{\partial S \, \partial V} \, dS_1 \, dV_1 + \frac{\partial^2 U_1}{\partial V^2} \, dV_1^2 \right].$$

Since T_0 and P_0 are fixed, this expression can be recast in the more suggestive form

$$dG = \frac{1}{2} \left[\frac{\partial^2 U_1}{\partial S^2} \, dS_1^2 + 2 \frac{\partial^2 U_1}{\partial S \, \partial V} \, dS_1 \, dV_1 + \frac{\partial^2 U_1}{\partial V^2} \, dV_1^2 \right], \tag{1.51}$$

so that a stable equilibrium demands that

$$\frac{\partial^2 U_1}{\partial S^2} \, dS_1^2 + 2 \frac{\partial^2 U_1}{\partial S \, \partial V} \, dS_1 \, dV_1 + \frac{\partial^2 U_1}{\partial V^2} \, dV_1^2 > 0. \tag{1.52}$$

This condition translates into the following inequalities for the first coefficient and the discriminant:

$$\frac{\partial^2 U_1}{\partial S^2} > 0,$$
$$\frac{\partial^2 U_1}{\partial S^2} \frac{\partial^2 U_1}{\partial V^2} - \left(\frac{\partial^2 U_1}{\partial S \, \partial V} \right)^2 > 0, \tag{1.53}$$

and taking into account that

$$\left(\frac{\partial^2 U_1}{\partial S^2} \right)_V = \left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V}, \tag{1.54}$$

the first condition that one can extract from the inequality is

$$C_V > 0. \tag{1.55}$$

One can then recast the second inequality of Eqs. (1.53) in the form

$$\frac{\partial(T,P)}{\partial(S,V)} \equiv \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial P}{\partial V}\right)_S - \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial P}{\partial S}\right)_V < 0, \tag{1.56}$$

and having identified this expression with a Jacobian, one can apply the chain rule to turn it into

$$\frac{\frac{\partial(T,P)}{\partial(T,V)}}{\frac{\partial(S,V)}{\partial(T,V)}} \equiv \frac{\left(\frac{\partial P}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{T}{C_V}\left(\frac{\partial P}{\partial V}\right)_T < 0. \tag{1.57}$$

The second condition that follows from stability is therefore

$$\left(\frac{\partial P}{\partial V}\right)_T < 0. \tag{1.58}$$

This was also the missing information required to conclude that $C_P > C_V$ in Section 1.3.

1.6 Specific Heat and Compressibility

One can now deduce an important relation between the isothermal and isentropic compressibilities, defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \qquad \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S, \tag{1.59}$$

and the specific heats. Indeed, the identity

$$\frac{\partial(S,P)}{\partial(T,P)}\frac{\partial(T,V)}{\partial(S,V)} = \frac{\partial(T,V)}{\partial(T,P)}\frac{\partial(S,P)}{\partial(S,V)}, \tag{1.60}$$

which is implied by the chain rule of Jacobians, translates into the relation

$$\frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial P}\right)_S}, \tag{1.61}$$

which is equivalent to

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}. \tag{1.62}$$

Note that, as a result of Eqs. (1.44) and (1.46), this implies that for stable systems the isothermal compressibility is normally larger than the isentropic compressibility.

Another interesting relation links the isothermal compressibility to the chemical potential. Let us note that, *at a fixed temperature* (omitting for brevity the corresponding subscript in the next equation),

$$\left(\frac{\partial P}{\partial V}\right)_N = \frac{\partial(P,N)}{\partial(P,V)}\frac{\partial(P,V)}{\partial(V,N)} = -\left(\frac{\partial N}{\partial V}\right)_P\left(\frac{\partial P}{\partial N}\right)_V. \tag{1.63}$$

Now using

$$\left(\frac{\partial N}{\partial V}\right)_{P,T} = n \qquad (1.64)$$

and the last Maxwell relation in (1.28), one is led to

$$\left(\frac{\partial P}{\partial V}\right)_{N,T} = n\left(\frac{\partial \mu}{\partial V}\right)_{N,T}, \qquad (1.65)$$

or equivalently to

$$-V\left(\frac{\partial P}{\partial V}\right)_{N,T} = n^2\left(\frac{\partial \mu}{\partial n}\right)_{N,T}, \qquad (1.66)$$

since μ, an intensive function, depends on V via the combination $n = \frac{N}{V}$. Therefore, the isothermal compressibility and the chemical potential are related to one another according to

$$\frac{1}{\kappa_T} = n^2\left(\frac{\partial \mu}{\partial n}\right)_N. \qquad (1.67)$$

The stability condition $\kappa_T > 0$ thus guarantees that the chemical grows with the density n. Hence, adding a new particle becomes more costly as the gas becomes denser. The effect is naturally less significant for systems with larger κ_T, which are more easily compressible.

1.7 The Ideal Monatomic Gas

This system plays a central role in thermodynamics and statistical physics and will recur in the following chapters. It provides results of universal value for monatomic gases at high temperatures and small densities. The equation of state for the ideal gas is, as is well known,

$$PV = Nk_B T, \qquad (1.68)$$

while the specific heat at constant volume is

$$C_V = \frac{3}{2}Nk_B, \qquad (1.69)$$

and Eq. (1.44) then implies that

$$C_P = \frac{5}{2}Nk_B. \qquad (1.70)$$

The internal energy for this system is simply

$$U = \frac{3}{2}Nk_B T, \qquad (1.71)$$

and is independent of V at a given temperature. Consequently

$$dS = \frac{3}{2}Nk_B \frac{dT}{T} + \frac{P}{T}dV \qquad (1.72)$$

can be integrated to obtain

$$S = \frac{3}{2} N k_B \log\left(\frac{T}{T_0}\right) + N k_B \log\left(\frac{v}{N v_0}\right), \tag{1.73}$$

where the dependence on the specific volume v makes S properly extensive, a point that we shall elaborate upon in Chapter 2. The two reference values T_0 and v_0 make the arguments of the logarithms properly dimensionless, while also introducing an additive constant in S, which is so far arbitrary. In Chapter 2 we shall connect them to microscopic properties of the gas. Moreover, as we shall see in Chapter 8, polyatomic molecules behave in a similar fashion at room temperatures and small densities, but have different values of their specific heats.

Bibliographical Notes

More details on various aspects of thermodynamics can be found in many books listed in the bibliography, for instance in [16, 36] or in [54].

Problems

1.1 Show that

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV,$$

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV.$$

1.2 Compute the efficiency of an ideal Carnot cycle (Figure 1.2) performed by a perfect gas, which is defined, as is well known, by pair of isothermal curves and a pair of adiabatic ones.

1.3 Compute the efficiency of an ideal Joule cycle (Figure 1.2) performed by a perfect gas, which is defined by a pair of adiabatic curves, together with a pair of isobaric ones. Express it as a function of the constant $\gamma = \frac{C_P}{C_V}$ and of the ratio of the two pressures, P_2, and P_1, of the isobaric transformations.
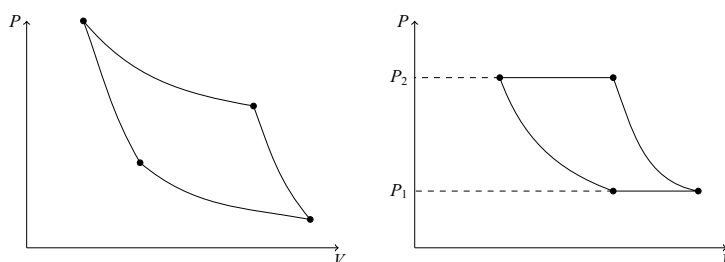

Figure 1.2 Reversible (Left) Carnot and (Right) Joule cycles.
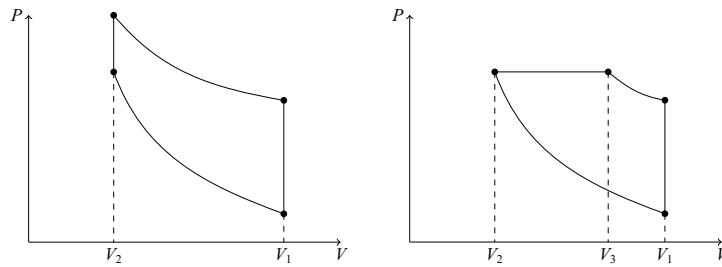
Figure 1.3   Reversible (Left) Otto and (Right) Diesel cycles.

1.4 Compute the efficiency of an ideal Otto cycle (Figure 1.3) performed by a perfect gas, which is defined by a pair of adiabatic curves and a pair of isochoric ones. Express it as a function of $\gamma = \frac{C_P}{C_V}$ and the compression rate $r = \frac{V_1}{V_2}$.

1.5 Compute the efficiency of an ideal Diesel cycle (Figure 1.3) performed by a perfect gas, which is defined by a pair of adiabatic curves, together with an isobaric and an isochoric one. Express it as a function of the constant $\gamma = \frac{C_P}{C_V}$ and the compression rates $r = \frac{V_1}{V_2}$ and $\alpha = \frac{V_3}{V_2}$.

1.6 Prove that two adiabatic curves in the (P, V) plane cannot intersect for any given substance.

1.7 Compute the variation of the Gibbs free energy along a reversible isothermal compression of a perfect gas of N particles, if the initial and final pressures are related by $P_2 = \sigma P_1$.

1.8 Consider a system whose chemical potential takes the form

$$\mu = k_B T \log P + g(T),$$

where $g(T)$ is a known function.

1. Derive the corresponding equation of state.
2. Compute the internal energy.

1.9 A system is described by the grand potential

$$\Omega = -\alpha V T^{\frac{5}{2}} e^{\frac{\mu}{k_B T}},$$

where α is a constant parameter.

1. Derive the corresponding equation of state
2. Obtain the chemical potential and the Helmholtz free energy.

1.10 Consider a system of N particles that, at a temperature T_0, performs work according to

$$L = N k_B T_0 \log \frac{V}{V_0}$$

during an isothermal expansion from a volume V to a volume V_0, and whose entropy is

$$S = Nk_B \frac{V_0}{V} \left(\frac{T}{T_0} \right)^\alpha.$$

1. Find the equation of state of the system.
2. Find the corresponding Helmholtz free energy.
3. Find the work performed by the system during an isothermal expansion at any given temperature T.

1.11 Consider a system that satisfies the relation $PV = Nk_B T_0$ at a given temperature T_0 and whose entropy is given by

$$S = 4Nk_B \left(\frac{T}{T_0} \right)^3 \log \left(\frac{P_0}{P} \right).$$

What is the equation of state for this system? Compute C_P and C_V explicitly, and verify that they are consistent with Eq. (1.44).

1.12 Consider two ideal monatomic gases with the same number of particles, N, initially at temperatures T_1 and T_2 and in mechanical equilibrium in nearby vessels separated by a moving insulating partition. What is the entropy change of the system when it reaches equilibrium after the partition is removed?

1.13 Consider two ideal monatomic gases containing the same number of particles, N, and held at the same temperature T but initially in different volumes V_1 and V_2 in nearby vessels. Compute the total entropy variation of the system when it reaches equilibrium after the partition between the two nearby vessels is removed. How can one interpret the result?

1.14 N molecules of an ideal gas contained in an isolated vessel are compressed adiabatically from a volume $2V$ to a volume V. A valve is then opened, so that the system returns to occupy the volume $2V$. Given the initial and final temperatures T_i and T_f, compute the total entropy variation of the system and the work performed by the gas. How can one interpret the result?

1.15 Consider a system of N particles for which

$$P = \frac{Nk_B T}{V} + f(T) \frac{N^2}{V^2}.$$

Compute the heat exchange Q and the work performed at constant T when the volume changes reversibly from V_1 to V_2.

1.16 Consider a system whose equation of state is

$$V = V_0 \, e^{\frac{T}{T_0} - \frac{P}{P_0}}.$$

1. Compute $C_P - C_V$ for the system.
2. Show that in this case C_V is only a function of T.

1.17 The efficiency of a refrigerator is defined as the ratio

$$\xi = \left| \frac{Q_2}{W} \right|$$

between the heat absorbed and the work needed to do it. Compute the efficiency of the Carnot cycle of Figure 1.2 working in reverse as a refrigerator between two temperatures T_1 and $T_2 > T_1$.

1.18 Repeat the preceding analysis for a refrigerator undergoing in a similar fashion the Joule cycle of Figure 1.2.

1.19 Repeat the preceding analysis for a refrigerator undergoing in a similar fashion the Otto cycle of Figure 1.3.

1.20 Repeat the preceding analysis for a refrigerator undergoing in a similar fashion the Diesel cycle of Figure 1.3.