On the thermodynamic equivalence of physical systems

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Abstract

Two different physical systems are said to be thermodynamically equivalent if one of the thermodynamic potentials of the first system is proportional to the corresponding potential of the second system after expressing the state variables of the first system in terms of those of the second by a transformation reversible throughout the state parameters’ full domain. The thermodynamic equivalence has a transitive nature so that physical systems divide into classes of thermodynamically equivalent systems that have similar phase diagrams. A thermodynamic equivalence class is formed by the ideal classical and quantum Fermi gases, whatever the dimension of the confining boxes, and the one dimensional hard rod gas. Another class is formed by the physical systems characterized by interactions that coincide by a scaling of the distance and the coupling constant. Finally the ideal Bose gases are not thermodynamically equivalent to the Fermi ones.

Keywords: Statistical thermodynamics, thermodynamic equivalence; hard-rod fluid; ideal classical gases; ideal quantum gases.
1 Introduction

The thermodynamic behaviour of an open physical system is fully determined by the knowledge of one of its thermodynamic potentials which depends on a triple of state variables (one of which, at least, extensive) chosen among the three pairs of conjugate variables \((V, p), (S, T)\) and \((N, \mu)\). Here, the extensive variables \(V, S\) and \(N\) respectively denote the volume, the entropy and the particle number of the sample while the intensive variables \(p, T\) and \(\mu\) are the pressure, the temperature and the chemical potential\[^1,^2\]. For instance, choosing \(V, S\) and \(N\) as state variables, the thermodynamic potential that fully determines the thermodynamic behavior of the system is the internal energy \(U(V, S, N)\) equal to

\[
U(V, S, N) = -p(V, S, N) V + T(V, S, N) S + \mu(V, S, N) N
\]

with

\[
p = p(V, S, N) = -\frac{\partial U(V, S, N)}{\partial V}, \tag{2}
\]

\[
T = T(V, S, N) = \frac{\partial U(V, S, N)}{\partial S}, \tag{3}
\]

\[
\mu = \mu(V, S, N) = \frac{\partial U(V, S, N)}{\partial N}. \tag{4}
\]

If one wishes to determine another thermodynamic potential, say the grand potential \(\Omega(V, T, \mu) = -p V\), one solves equaltions (3) and (4) with respect to \(S\) and \(N\) so as to get

\[
S = S(V, T, \mu) \quad \text{and} \quad N = N(V, T, \mu). \tag{5}
\]

After substituting these into equation (2) one finds the expression of the grand potential in terms of its natural variables, \(\Omega(V, T, \mu) = -p(V, T, \mu)V\).

\[
\Omega(V, T, \mu) = -p(V, T, \mu)V. \tag{6}
\]

In this way the transformation \((V, S, N) \to (V, T, \mu)\), defined by

\[
V \to V, \quad S \to S(V, T, \mu) \quad \text{and} \quad N \to N(V, T, \mu), \tag{7}
\]

allows one to describe the thermodynamic behaviour of the system using the grand potential instead of the internal energy.

Consider now two different physical systems A and B in thermodynamic equilibrium. One wonders on the implications of a reversible transformation between the state variables relevant to a thermodynamic potential of the
first system and the state variables of the same thermodynamic potential relevant to the second system. These transformations lead to the definition of the thermodynamic equivalence that in turns unifies the behaviour of different thermodynamic systems as it will be shown in the following section. Three examples of different physical systems that are thermodynamically equivalent are discussed sections 3–5. The last section also reports an example of two systems that are not thermodynamically equivalent. Finally, section 6 draws the final conclusions.

2 Thermodynamical equivalence

For definiteness let us refer to the grand potentials \( \Omega_A(V_A, T_A, \mu_A) \) and \( \Omega_B(V_B, T_B, \mu_B) \) of systems A and B and denote the transformation from \((V_B, T_B, \mu_B)\) of B to \((V_A, T_A, \mu_A)\) of A as

\[
\begin{align*}
V_B &\rightarrow V_A = V_{a,b}(V_B, T_B, \mu_B) \equiv V_B v_{a,b}(T_B, \mu_B), \quad (8) \\
T_B &\rightarrow T_A = T_{a,b}(V_B, T_B, \mu_B) \equiv t_{a,b}(T_B, \mu_B), \quad (9) \\
\mu_B &\rightarrow \mu_A = \mu_{a,b}(V_B, T_B, \mu_B) \equiv \bar{\mu}_{a,b}(T_B, \mu_B). \quad (10)
\end{align*}
\]

It is noted that the functional forms reported in the rightmost members of the above three relations are dictated by the extensive or intensive nature of the considered variables. The transformation is required to be endowed of continuous partial derivatives at least up to the second order, to be reversible and to be physically meaningful. The last condition implies that \( v_{a,b}(T_B, \mu_B) \) and \( t_{a,b}(T_B, \mu_B) \) must be strictly positive and the second that the codomains of functions (8)-(10) coincide with the physical ranges of variables \( V_A, T_A \) and \( \mu_A \). Denoting the inverse functions of \( t_{a,b}(T_B, \mu_B) \) and \( \bar{\mu}_{a,b}(T_B, \mu_B) \) as \( t_{b,a}(T_A, \mu_A) \) and \( \bar{\mu}_{b,a}(T_A, \mu_A) \), the inverse transformation of equations (8)-(10) reads

\[
\begin{align*}
V_A &\rightarrow V_B = V_{b,a}(V_A, T_A, \mu_A) \equiv V_A v_{b,a}(T_A, \mu_A), \quad (11) \\
T_A &\rightarrow T_B = T_{b,a}(V_A, T_A, \mu_A) \equiv t_{b,a}(T_A, \mu_A), \quad (12) \\
\mu_A &\rightarrow \mu_B = \mu_{b,a}(V_A, T_A, \mu_A) \equiv \bar{\mu}_{b,a}(T_A, \mu_A). \quad (13)
\end{align*}
\]

where

\[
v_{b,a}(T_A, \mu_A) \equiv 1/v_{a,b}(T_B, \mu_B) = 1/v_{a,b}(t_{b,a}(T_A, \mu_A), \bar{\mu}_{b,a}(T_A, \mu_A)). \quad (14)
\]
Applying the state variable transformations (8)-(10) to the grand potential of system A, one obtains the new function $\Omega_{A,B}$ defined as

$$\Omega_{A,B}(V_B, T_B, \mu_B) \equiv \Omega_A(V_{A,B}(V_B, T_B, \mu_B), T_{A,B}(V_B, T_B, \mu_B), \mu_{A,B}(V_B, T_B, \mu_B)).$$

(15)

Systems A and B are said to be thermodynamically equivalent if function $\Omega_{A,B}$ is proportional to the grand potential of system B, i.e.

$$\Omega_{A,B}(V_B, T_B, \mu_B) = C_{AB} \Omega_B(V_B, T_B, \mu_B),$$

(16)

$C_{AB}$ being a real positive constant.

From this definition immediately follows that the thermodynamic equivalence may occurs if:

a) the codomains of the two grand potentials $\Omega_A$ and $\Omega_B$ become identical by a scale transformation of one of them, and

b) the state diagrams have a similar shape in the sense that the state diagram of system A converts into that of system B by the transformation (8)-(10). [In fact, the state diagram of A is determined by the state variable points where the second order partial derivatives of $\Omega_A$ are discontinuous. Equality (16) and the assumed continuity of the partial derivatives of the state variable transformation imply a discontinuous behaviour of the relevant second order derivatives of $\Omega_B$.]

Besides, the thermodynamic equivalence definition implies that:

c) if physical system A is thermodynamically equivalent to B and this is thermodynamically equivalent to system C, then systems A and C also are thermodynamically equivalent. In fact, thermodynamic equivalence of B and C implies the existence of a reversible transformation: $V_C \rightarrow V_B = V_{B,C}$, $T_C \rightarrow T_B = T_{B,C}$ and $\mu_C \rightarrow \mu_B = \mu_{B,C}$ [where $V_{B,C}$, $T_{B,C}$ and $\mu_{B,C}$ denote functions that depend on $V_C$, $T_C$ and $\mu_C$] such that

$$\Omega_B(V_{B,C}, T_{B,C}, \mu_{B,C}) = \Omega_{B,C}(V_C, T_C, \mu_C) = C_{BC} \Omega_C(V_C, T_C, \mu_C).$$

(17)

On the other hand, the state variable transformation

$$V_C \rightarrow V_A = V_{A,C} \equiv V_{A,B}(V_{B,C}, T_{B,C}, \mu_{B,C}),$$

(18)

$$T_C \rightarrow T_A = T_{A,C} \equiv T_{A,B}(V_{B,C}, T_{B,C}, \mu_{B,C}),$$

(19)

$$\mu_C \rightarrow \mu_A = \mu_{A,C} \equiv V_{A,B}(V_{B,C}, T_{B,C}, \mu_{B,C})$$

(20)

exists and is reversible. Applying this transformation to $\Omega_A$ and using equations (16) and (17), one gets

$$\Omega_A(V_{A,C}, T_{A,C}, \mu_{A,C}) = \Omega_A(V_{A,B}, T_{A,B}, \mu_{A,B}) \bigg|_{V_B=V_{B,C}, T_B=T_{B,C}, \mu_B=\mu_{B,C}} = (21)$$

$$C_{AB} \Omega_B(V_B, T_B, \mu_B) \bigg|_{V_B=V_{B,C}, T_B=T_{B,C}, \mu_B=\mu_{B,C}} = C_{AB} C_{BC} \Omega_C(V_C, T_C, \mu_C),$$

(22)
which proves the thermodynamic equivalence of A and C if A is equivalent to B and B to C. This property implies that the totality of the physical systems splits into different classes of thermodynamically equivalent systems. The thermodynamic equivalence also implies that each thermodynamic quantity of system A is related to the corresponding quantity of system B in a known way. Just to give an example, consider the entropies $S_A$ and $S_B$ of systems A and B. They are given by the relations $S_A = -\frac{\partial \Omega_A(V_A, T_A, \mu_A)}{\partial T_A}$ and $S_B = -\frac{\partial \Omega_B(V_B, T_B, \mu_B)}{\partial T_B}$. Taking the $T_B$ derivative of equations (15)-(16) and recalling that the pressure and the system particle number are respectively given by

$$p(V, T, \mu) = -\frac{\partial \Omega(V, T, \mu)}{\partial V},$$

$$N(V, T, \mu) = -\frac{\partial \Omega(V, T, \mu)}{\partial \mu},$$

one finds

$$C_{AB} S_B(V_B, T_B, \mu_B) = S_A(V_A, T_A, \mu_A) \frac{\partial t_{a,b}}{\partial T_B} +$$

$$p_A(V_A, T_A, \mu_A) V_A \frac{\partial v_{a,b}}{\partial T_B} + N_A(V_A, T_A, \mu_A) \frac{\partial \mu_{a,b}}{\partial T_B},$$

so that the entropy of system B is a linear combination of the entropy, the pressure and the number particle of system A and the coefficients of the linear combination are known since they are appropriate derivatives of the state variable transformation. The same property holds true for the pressure and the system particle number. Similar inter-relations exist for other quantities as the specific heats at fixed particle number and at constant volume or at constant pressure, even though they become more involved since these quantities are related to higher order derivatives of the grand potentials.

It is observed that the validity of equation (16) is not sufficient to determine the coordinate transformation. In fact, if one tries to determine the transformation by expanding around a particular thermodynamic state, one realizes that the number of the involved unknown derivatives is larger than the number of the equations. However if one identifies two of the state variables by setting, say, $V_A = V_B = V$ and $T_A = T_B = T$, then equation (16) may be sufficient for expressing $\mu_A$ in terms of $\mu_B$ and $T$. This result does not imply that two physical systems always are thermodynamic equivalent because it is not ensured that the resulting transformation is invertible and spans the physical ranges of the transformed state variables.

It is noted that, in defining the thermodynamic equivalence, one has to choose one of the thermodynamic potentials. One wonders if, assuming that two systems are thermodynamically equivalent with respect to, say, the grand
potentials, they also are equivalent with respect to another thermodynamic potential. In section 3 it is reported a case where this happens, but the general answer is as yet unknown. Finally, the reported definition of thermodynamic equivalence could be made less restrictive modifying condition (16) as follows

$$
\Omega_{A,B}(V_B, T_B, \mu_B) = C_{AB}(T_B, \mu_B)\Omega_B(V_B, T_B, \mu_B) + A_{AB}(V_B, T_B, \mu_B), \tag{25}
$$

where $C_{AB}$ and $A_{AB}$ are known functions of the reported state variables. This new definition however looks too much general to become nearly trivial in the sense that any transformation of the state variables of two different physical systems, provided it is invertible through out the state variable full ranges, leads to their thermodynamic equivalence. Further, properties (a) and (b) no longer apply to definition (25). For this reason the following analysis will be confined to definition (16).

3 The hard rod gas in one dimension and the ideal classical gas in any dimension

This section reports a first set of physical systems that are thermodynamically equivalent. They are the classical ideal gases in any space dimension $D$ and the hard rod gas in one dimension. Consider first the pair formed by the one dimensional and the three dimensional classical ideal gases. The grand potential of the classical ideal gas, confined into a box of length side $L$ and contained into a space of dimension $D (= 1, 2, 3)$, reads

$$
\Omega_{ig,D}(V_D, T, \mu_{ig}) = -k_B T V_D e^{\mu_{ig}/k_B T} - \lambda_D, \tag{26}
$$

with $V_D = L^D$ and

$$
\lambda \equiv h/\sqrt{2\pi mk_B T}, \tag{27}
$$

denoting the de Broglie length, $h$ and $k_B$ the Planck and the Boltzmann constants and $m$ the particle mass. For later reference it is convenient to report here also the expressions of the particle number density and the pressure, respectively given by

$$
n_{ig}(T, \mu_{ig}) = -\frac{1}{V_D} \frac{\partial \Omega_{ig,D}(L, T, \mu_{ig})}{\partial \mu_{ig}} = \frac{e^{\mu_{ig}/k_B T}}{\lambda_D}, \tag{28}
$$

and

$$
p_{ig}(T, \mu_{ig}) = -\frac{\partial \Omega_{ig,D}(L, T, \mu_{ig})}{\partial V_D} = k_B T n_{ig}(T, \mu_{ig}). \tag{29}
$$
To prove the thermodynamic equivalence of the considered ideal gases, one writes the right hand side of equation (26) using definition (27) as

\[- \frac{k_B(2\pi m)^{D/2}}{\hbar^D}T_D^{D/2+1}V_D e^{\mu_{ig,D}/k_BT_D}.\]  

(30)

It is clear that the transformation

\[T_1 = T_3^{5/3}, \quad V_1 = V_3/l_0^2, \quad \text{and} \quad \mu_{ig,1} = \mu_{ig,3}T_3^{2/3},\]  

(31)

where \(l_0\) denotes an arbitrarily chosen length, is invertible and continuous with all its partial derivatives. Once it is applied to \(\Omega_{ig,1}(V_1, T_1, \mu_{ig,1})\) one finds that

\[\Omega_{ig,1}(V_1, T_1, \mu_{ig,1}) = \frac{\hbar}{2\pi m l_0^2}\Omega_{ig,3}(V_3, T_3, \mu_{ig,3}),\]  

(32)

which is equation (16) with \(C_{A,B} = \hbar^2/2\pi ml_0^2\). Thus, the thermodynamic equivalence of the one-dimensional and the three-dimensional classical ideal gases is proved. By the same procedure one proves the thermodynamic equivalence of the one-dimensional and the two-dimensional ideal gases. In this way, by the transitiveness of the thermodynamic equivalence [see property (c) below equation (16)], one concludes that the \(D\)-dimensional ideal classical gases, whatever the positive integer \(D\) value, form a class of thermodynamic equivalent systems.

To prove that the one-dimensional ideal gas is thermodynamically equivalent to the one-dimensional hard rod gas of particles of mass \(m\) and length \(\sigma\), it is first recalled that the last system is characterized by the interaction potential \(v_{hr}(r)\) defined as \(v_{hr}(r) = 0\) if \(r > \sigma\) and \(v_{hr}(r) = \infty\) if \(0 < r < \sigma\). Rayleigh[3] and Tonk[4] have since long determined the equation of state of the one dimensional hard rod system. More recently Robledo and Rowlinson[5] have determined the full thermodynamic behaviour of this system within the grand canonical framework paying great attention to the behaviour of the one particle distribution function close to the system walls. The mentioned thermodynamic equivalence between the ideal gas and the hard rod gas holds only true in the thermodynamic limit, \(i.e.\) when the walls are infinitely far away. The grand partition function of the hard rod gas, confined to a box of size \(L\), (after correcting a misprint present in the corresponding expression of reference [5]) is

\[\Xi_{hr}(L, T, \mu_{nr}) = \sum_{k=0}^{[L/\sigma]} \frac{\zeta_{hr}}{k!} (L - k\sigma)^k.\]  

(33)

with

\[\zeta_{hr} \equiv e^{\mu_{hr}/(k_BT)} / \lambda_i\]  

(34)
and \( [L/\sigma] \) equal to the integer part of \( L/\sigma \). The mean particle number of the particles \( \langle N \rangle_L \) is

\[
\langle N \rangle_L = \zeta_{hr} \frac{\Xi_{hr}(L - \sigma, T, \mu_{hr})}{\Xi_{hr}(L, T, \mu_{hr})} (L - \sigma - \langle N \rangle_{L-\sigma}),
\]

(35)

so that, in the limit \( L \to \infty \) with \( \langle N \rangle_L / L = n_{hr} \) fixed \( [n_{hr} \) denoting the bulk particle number density of the hard rod fluid], one finds that

\[
\lim_{L \to \infty} \zeta_{hr} \frac{\Xi_{hr}(L - \sigma, T, \mu_{hr})}{\Xi_{hr}(L, T, \mu_{hr})} = \frac{n_{hr}}{1 - \sigma n_{hr}}.
\]

(36)

It also results that

\[
\frac{\partial \log \Xi_{hr}}{\partial L} = \zeta_{hr} \frac{\Xi_{hr}(L - \sigma, T, \mu_{hr})}{\Xi_{hr}(L, T, \mu_{hr})}.
\]

(37)

Using equation (36), the above relation can be integrated to yield

\[
\log (\Xi_{hr}(L, T, \mu_{hr})) = \frac{L n_{hr}}{1 - \sigma n_{hr}} + \text{const},
\]

(38)

which in turns implies that

\[
\Xi_{hr}(L - \sigma, T, \mu_{hr})/\Xi_{hr}(L, T, \mu_{hr}) = \exp \left( -\sigma n_{hr}/(1 - \sigma n_{hr}) \right).
\]

This result converts equation (36) into

\[
\zeta_{hr} = \frac{n_{hr}}{1 - \sigma n_{hr}} e^{\frac{n_{hr} \sigma}{1 - \sigma n_{hr}}}
\]

(39)

that allows one to relate the chemical potential \( \mu_{hr} \) to the particle number density \( n_{hr} \). Putting \( \text{const} = 0 \) in equation (38) to ensure the extensiveness of the function, one finds that the grand potential of the hard rod system is

\[
\Omega_{hr}(L, T, n_{hr}) = -k_B T \log (\Xi_{hr}(L, T, \mu_{hr})) = -k_B T \frac{L n_{hr}}{1 - \sigma n_{hr}}.
\]

(40)

This \( \Omega_{hr} \) expression depends on \( n_{hr} \), while it is important to know \( \Omega_{hr} \) in terms of \( \mu_{hr} \) in order to derive from it the other thermodynamic quantities. This can easily be realized using equation (39) to express \( n_{hr} \) in terms of \( \mu_{hr} \). To this aim one recalls that the solution, with respect to \( x \), of the equation \( y = xe^x \) is a transcendental function known as Lambert’s function\(^6\) and

8
denoted as \( x = W(y) \). This function also is the solution of the following differential equation

\[
W'(y) = \frac{W(y)}{y(1 + W(y))} = \frac{e^{-W(y)}}{1 + W(y)}
\]  

(41)

with the boundary condition \( W(0) = 0 \). Hence, the solution of equation \((39)\) with respect to \( n_{hr} \) is

\[
n_{hr}(T, \mu_{hr}) = \frac{W(\sigma e^{\mu_{hr}/k_B T}/\lambda)}{\sigma(1 + W(\sigma e^{\mu_{hr}/k_B T}/\lambda))}.
\]  

(42)

Recalling that \( W(y) \approx \log(y) \) as \( y \to \infty \), this equation implies that \( n_{hr} \to 1/\sigma \) as \( \mu_{hr} \to \infty \) and \( 1/\sigma \) clearly represents the system density at the closest packing. The substitution of \((42)\) within equation \((40)\) yields the expression of the hard rod grand potential in terms of its natural variables, \( i.e. \)

\[
\Omega_{hr}(L, T, \mu_{hr}) = -k_B T \frac{L}{\lambda} W(\sigma e^{\mu_{hr}/k_B T}/\lambda).
\]  

(43)

[The use of the same \( \Omega_{hr} \) symbol here and in equation \((40)\) is dictated by the sake of notational simplicity even though it is not mathematically correct. The same convention will be used later on.] The interaction of the hard rod fluid vanishes in the limit \( \sigma \to 0 \) so that the hard rod fluid must behave as the ideal gas in the aforesaid limit. Since the Lambert function is such that \( W(y) \approx y \) as \( y \to 0 \) one immediately realizes that

\[
\lim_{\sigma \to 0} \Omega_{hr}(L, T, \mu_{hr}) = -k_B T L e^{\mu_{ig}/k_B T}/\lambda = \Omega_{ig}(L, T, \mu_{ig})
\]  

(44)

once one sets \( \mu_{hr} = \mu_{ig} \), and the identical behaviour of the two systems in the limit \( \sigma \to 0 \) is proved.

The interesting point is that the hard rod and the ideal gases are thermodynamically equivalent if \( \sigma > 0 \). Consider, in fact, the following transformation of the state variables of the two systems

\[
T_{ig} = T_{hr} = T, \quad L_{ig} = L_{hr} = L
\]

\[
\mu_{ig} = \mu_{ig}(T, \mu_{hr}) = k_B T \left( \log(\lambda/\sigma) + \log(W(\lambda e^{\mu_{hr}/k_B T}/\sigma)) \right).
\]  

(45)

It is a reversible transformation because the last equality can be inverted throughout the full range \((-\infty, \infty)\) of \( \mu_{hr} \) to yield

\[
\mu_{hr} = \mu_{hr}(T, \mu_{ig}) = \mu_{ig} + \frac{k_B T}{\lambda} \frac{\mu_{ig}}{e^{\mu_{ig}/k_B T}}.
\]  

(46)
Once transformation (45) is applied to equation (26) one finds that

$$\Omega_{ig}(L, T, \mu_{ig}(T, \mu_{hr})) = \Omega_{hr}(L, T, \mu_{hr}),$$

that is equation (16) with $C_{AB} = 1$. In this way the thermodynamic equivalence of the one dimensional hard rod and ideal gases is proved. Due to property (c), one concludes that the D-dimensional ideal gases and the one dimensional hard rod gas form a class of thermodynamically equivalent systems.

The substitution of (45) into equation (28) and the use of equation (42) imply that the particle number densities of the two systems are related by

$$n_{ig} = \frac{n_{hr}}{1 - \sigma n_{hr}}.$$

This equation makes it evident that, as $n_{hr}$ ranges over the allowed physical range $[0, 1/\sigma]$, $n_{ig}$ ranges over its physical range, namely the positive half-axis. The equation of state of the hard rod system is obtained by taking the derivative of $\Omega_{hr}$ with respect to $(-L)$. It can directly be expressed in terms of variables $T$ and $n_{hr}$ derivating equation (40). One finds

$$p_{hr} = k_B T \frac{L n_{hr}}{1 - \sigma n_{hr}},$$

and, once one uses here relation (48), it coincides with that of the one-dimensional ideal gas $p_{ig} = k_B T n_{ig}$.

The entropy expressions are easily obtained from the grand potential expressions. For the hard rods fluid one finds

$$S_{hr}(L, T, \mu_{hr}) = \frac{L k_B}{\sigma} W(\sigma \sqrt{\mu_{hr}/(k_B T)}) \left[ \frac{3}{2} + W(\sigma \sqrt{\mu_{hr}/(k_B T)}) \right] - \frac{\mu_{hr}}{k_B T} \frac{1}{1 + W(\sigma \sqrt{\mu_{hr}/(k_B T)})},$$

which, in terms of $n_{hr}$, reads

$$S_{hr}(L, T, n_{hr}) = k_B L n_{hr} \left( 3/2 - \log(\lambda n_{hr}/(1 - n_{hr} \sigma)) \right).$$

For the one-dimensional ideal gas one gets

$$S_{ig}(L, T, \mu_{ig}) = k_B L m \sqrt{\pi/2} e^{\mu_{ig}/k_B T} \left( \frac{3}{2} - \frac{\mu_{ig}}{h \sqrt{k_B m T}} \right)$$

$$= k_B L n_{ig} \left( 3/2 - \log(\lambda n_{ig}) \right).$$
The substitution of transformation (45) into (52) does not convert the ideal gas entropy in that of the hard rods. In fact, the two entropies are related by the relation [see equation (24)]

$$S_{hr}(L, T, \mu_{hr}) = S_{ig}(L, T, \mu_{ig}(T, \mu_{hr})) \frac{\partial \mu_{ig}(T, \mu_{hr})}{\partial T},$$  \hspace{1cm} (53)

because the $\mu_{ig}$ transformation, given by (45c), depends also on $T$.

The expressions of the Helmotz free energies and internal energies of the two systems are now reported for completeness. The free energies are

$$F_{hr}(L_{hr}, T_{hr}, N_{hr}) = -k_B T_{hr} N_{hr} \left(1 - \log(\lambda n_{hr} / (1 - n_{hr} \sigma)) \right),$$ \hspace{1cm} (54)

and

$$F_{ig}(L_{ig}, T_{ig}, N_{ig}) = -k_B T_{ig} N_{ig} \left(1 - \log(\lambda n_{ig}) \right),$$ \hspace{1cm} (55)

and the internal energies read

$$U_{hr}(L_{hr}, S_{hr}, N_{hr}) = \frac{\hbar^2}{4\pi m} \frac{n_{hr}^3}{(1 - \sigma n_{hr})^2} e^{-3+2S_{hr}/(k_B N_{hr})}$$ \hspace{1cm} (56)

and

$$U_{ig}(L_{ig}, S_{ig}, N_{ig}) = \frac{\hbar^2}{4\pi m} n_{ig}^3 e^{-3+2S_{ig}/(k_B N_{ig})}.$$ \hspace{1cm} (57)

One easily verifies that the following reversible transformation of the state variables

$$N_{ig} = N_{hr} = N, \quad T_{ig} = T_{hr} = T, \quad L_{ig} = L_{ig}(L_{hr}, N) = L_{hr} - N \sigma,$$ \hspace{1cm} (58)

(with the bound $N < L_{hr}/\sigma$) yields

$$F_{ig}(L_{ig}(L_{hr}, N), T, N) = F_{hr}(L_{hr}, T, N).$$ \hspace{1cm} (59)

This relation proves the thermodynamic equivalence of the two systems making use of the Helmotz free energies.

If one considers, as thermodynamic potentials, the internal energies [see equations (56) and (57)], it is straightforward to show that the following reversible state variable transformation

$$L_{ig} = L_{hr} = L, \quad n_{ig} = \frac{n_{hr}}{(1 - \sigma n_{hr})^{2/3}}, \quad S_{ig}/n_{ig} = S_{hr}/n_{hr}$$

yields that

$$U_{ig}(L_{ig}, S_{ig}, N_{ig}) = U_{hr}(L_{hr}, S_{hr}, N_{hr}).$$ \hspace{1cm} (60)
i.e. the internal energies also are thermodynamically equivalent. Equations (59) and (60) suggest that if the grand potentials are thermodynamically equivalent the same happens to the the other thermodynamic potentials, even though a general proof of this conjecture is still lacking.

Before concluding the section, we report two properties of the hard rod fluid. The first concerns the heat capacities at fixed particle number and at fixed volume or at fixed pressure. The first is easily derived from expression (51) and the second from the same expression after expressing $L_{hr}$ in terms of $p_{hr}$ by equation (49). In this way one respectively finds

$$C_{hr,V} = k_B N_{hr}/2 \quad \text{and} \quad C_{hr,p} = 3k_B N_{hr}/2,$$

which have the same analytic forms of the ideal gas heat capacities, i.e. $C_{ig,V} = k_B N_{ig}/2$ and $C_{ig,p} = 3k_B N_{ig}/2$.

The second property concerns the existence of the proportionality relation between the grand potential and the internal energy, i.e.

$$\Omega_{hr}(L_{hr}, S_{hr}, N_{hr}) = \frac{1}{1 - \sigma n_{hr}} U_{hr}(L_{hr}, S_{hr}, N_{hr})$$

This relation is obtained by substituting the temperature expression $T = -\partial U/\partial S$, resulting from equation (56), into equation (40) and then by comparing the result with (56). For the ideal gas the equivalent relation is [8] $\Omega_{ig} = -\frac{1}{2} U_{ig}$ that differs from (62) because the proportionality coefficient is here strictly constant while it depends on the particle number density for the hard rod gas.

4 Systems having the same scaled interaction

The systems considered in the previous section are characterized by interactions that coincide if the inter-particle distance exceeds $\sigma$. In this section one considers the cases where the interactions have a similar behaviour throughout the full range of distances in so far they have the form $gV(r/\sigma)$ with $V(r)$ fixed and $g$ and $\sigma$ variable. Hence, one assumes that system A is made up of particles of mass $m_A$, diameter $\sigma_A$, and interaction $g_A V(r/\sigma_A$) and system B of particles of mass $m_B$, diameter $\sigma_B$ and interaction $g_B V(r/\sigma_B)$. The two systems are thermodynamically equivalent. In fact, the classical grand canonical partition function of system A, after integrating over the particles’
momentums, is
\[
\Xi_A(V_A, T_A, \mu_A) \equiv \sum_{k=0}^{\infty} \frac{z_A^k (2\pi m_A k_B T_A)^k}{k! h^{3k}} \times \int_{V_A} \ldots \int_{V_A} e^{-\frac{g_B}{k_B T_A} \sum_{1 \leq i < j \leq k} V(r_{i,j}/\sigma_A)} d^N r \tag{63}
\]
with
\[
z_A \equiv e^{\mu_A/k_B T_A}. \tag{64}
\]
The corresponding grand potential is
\[
\Omega_A(V_A, T_A, \mu_A) = -k_B T_A \log(\Xi_A(V_A, T_A, \mu_A)). \tag{65}
\]

The grand partition function of system B is
\[
\Xi_B(V_B, T_B, \mu_B) \equiv \sum_{k=0}^{\infty} \frac{z_B^k (2\pi m_B k_B T_B)^k}{k! h^{3k}} \times \int_{V_B} \ldots \int_{V_B} e^{-\frac{g_B}{k_B T_B} \sum_{1 \leq i < j \leq k} V(r_{i,j}/\sigma_B)} d^N r. \tag{66}
\]
Putting \(\sigma_{AB} \equiv \sigma_A/\sigma_B\) (and \(\sigma_{BA} \equiv \sigma_B/\sigma_A\)) and performing the following change of the integration variables \(r_i \rightarrow \sigma_{AB} r'_i\), the configuration integral present in the \(k\)th term of series (63) becomes
\[
\sigma_{AB}^{3k} \int_{V_A \sigma_{BA}} \ldots \int_{V_A \sigma_{BA}} e^{-\frac{g_B}{k_B T_A} \sum_{1 \leq i < j \leq k} V(r'_{i,j}/\sigma_B)} d^N r'. \tag{68}
\]
At this point one easily verifies that the state variable transformation
\[
V_B = V_B(V_A) \equiv V_A \sigma_{BA}^3, \quad T_B = T_B(T_A) \equiv g_B T_A/g_A, \quad \text{and} \quad z_B = z_A \frac{m_A^{3/2} \sigma_A^3 g_B^{3/2}}{m_B^{3/2} \sigma_B^3 g_A^{3/2}}, \tag{69}
\]
the last being equivalent to
\[
\mu_B = \mu_B(T_A, \mu_A) \equiv \frac{g_B}{g_A} \left[ \mu_A + \frac{3}{2} k_B T_A \log \left( \frac{m_A g_A \sigma_A^2}{m_B g_B \sigma_B^2} \right) \right], \tag{70}
\]
is reversible and yields
\[
\Xi_B(V_B(V_A), T_B(T_A), \mu_B(T_A, \mu_A)) \equiv \Xi_A(V_A, T_A, \mu_A). \tag{71}
\]
This, in turns, implies that

$$\Omega_B(V_B(V_A), T_B(T_A), \mu_B(T_A, \mu_A)) = (g_B/g_A) \Omega_A(V_A, T_A, \mu_A).$$  \(72\)

In this way, according to equation \(16\) with \(C_{BA} \equiv g_B/g_A\), the thermodynamic equivalence of systems A and B is proved. This result shows that a class of equivalent thermodynamic systems is formed by those systems such that each of them is formed by particles, of a given mass and diameter, which interact with a potential having a particular coupling value and a fixed shape. Hence, the systems interacting with a Lennard-Jones potential form a class of thermodynamically equivalent systems. The same happens for the Coulombic systems. It is noted that the systems, which are thermodynamically equivalent under the variable transformations \(69\) and \(70\), also obey the law of corresponding states\[^1\].

### 5 The ideal quantum gases

It is now shown that, within a space of dimension \(D\), the ideal classical gas is thermodynamically equivalent to the ideal Fermi one and is not thermodynamically equivalent to the ideal Bose one. To this aim it is first recalled that Lee\[^9\] showed that the grand potential expressions of the two ideal quantum gases can be expressed in terms of the same mathematical functions as follows

$$\Omega_{B,D}(V_B, T_B, \mu_B) = -\left[\frac{g_B V_B k_B T_B}{\lambda^D}\right] \text{Li}_{D/2+1}(z_B),$$  \(73\)

$$\Omega_{F,D}(V_F, T_F, \mu_F) = \left[\frac{g_F V_F k_F T_F}{\lambda^D}\right] \text{Li}_{D/2+1}(-z_F)$$  \(74\)

Here suffices \(B\) and \(F\) respectively refer to the Bose and the Fermi gas, \(g_B = 2s_B + 1\) with \(s_B\) equal to the particle spin, \(\lambda = h/\sqrt{2\pi mk_B T}\), \(V_B = V_F = L^D\) with \(L\) equal to the length of the confining box edge and \(D\) equal to the space dimensionality. Further, \(z_B( = e^{\mu_B/k_B T})\) and \(z_F( = e^{\mu_F/k_B T})\) are the Bose and Fermi gas fugacities. Finally, \(\text{Li}_s(z)\) is the so-called polylogarithmic function\[^10\] of index \(s\) that is simply related\[^11\] to \(\Phi(z, s, a)\), the Lerch function, by the relation

$$\text{Li}_s(z) = z \Phi(z, s, 1),$$  \(75\)

so that the ideal Fermi and Bose grand potentials can also be expressed\[^12\] in terms of the Lerch function. This is defined as\[^11\]

$$\Phi(z, s, a) \equiv \frac{1}{\Gamma(s)} \int_0^\infty \frac{t^{s-1} e^{-at}}{1 - z e^{-t}} dt$$  \(76\)
for Re$(a) > 0$, Re$(s) > 0$ and Re$(z) < 1$. It obeys the three properties

$$
\Phi(z, s, a) = \sum_{p=0}^{\infty} \frac{z^p}{(p+a)^s} \quad \text{if} \quad |z| < 1,
$$

(77)

and

$$
\Phi(z, s - 1, a) = (a + z \frac{\partial}{\partial z}) \Phi(z, s, a)
$$

(78)

and

$$
\Phi(z, s + 1, a) = -\frac{1}{s} \frac{\partial}{\partial a} \Phi(z, s, a).
$$

(79)

The reported integral shows that the Lerch function is analytic in the complex $z$ plane cut along the real axis from one to $\infty$. Further, equation (76) shows that $\Phi(z, s, a) > 0$ as $z$ ranges over $(-\infty, 1)$. From this property and equation (75) it follows that $\text{Li}_s(z)$ (with $s > 1$) monotonously increases as $z$ goes from $-\infty$ to 1. The behaviour of the $\text{Li}_s(z)$s for $s = \frac{3}{2}, 2, \frac{5}{2}$, the values associated to $D = 1, 2$ and 3, are shown in Figure 1 for $-\infty < z < 1$. Further, the leading behaviour of $\text{Li}_s(z)$, as $z \to 1^{-}$, is

$$
\text{Li}_s(z) \approx \frac{\zeta(s)}{\Gamma(1 + s)} \log |z|, \quad \text{as} \quad z \to -\infty.
$$

(81)

This behaviour is obtained using Jonquières’s relation (see equation (1.11.1.16) of reference [11]) and the asymptotic expansion of the Hurwitz function $\zeta(a, b)$ as $b \to \infty$ in the complex plane (see equation (25.11.43) of reference [6]).

At this point, for each $D$ value, the proof of the thermodynamic equivalence of the classical ideal gas and the ideal Fermi gas is straightforward. In fact, consider the state variable transformation

$$
T_{ig} = T_F = T, \quad V_{ig} = V_F = V \quad \text{and} \quad z_{ig} = -\text{Li}_{D/2+1}(-z_F),
$$

(82)

the last relation being equivalent to

$$
\mu_{ig} = \mu_{ig}(\mu_F, T) \equiv k_B T \log(-\text{Li}_{D/2+1}(-\epsilon_F/k_B T)).
$$

(83)
Figure 1: The curves in colours are the plots of $\text{Li}_s(z)$ for $s = 5/2$ (blue), $s = 2$ (red) and $s = 3/2$ (magenta) within the range $-\infty < z < 1$. The curves are broken within the negative $z$ half-axis and continuous within the range $0 \leq z < 1$ to make it more evident that they respectively are the plots of $\text{Li}_s(-z_F)$ with $z_F > 0$ and of $\text{Li}_s(z_B)$ with $0 \leq z_B < 1$. Note that the $\text{Li}_s(z)$ limits are finite as $z \to 1$. The black broken and continuous straight lines are the plots of $-z_{ig}$ and $z_{ig}$ as $\mu_{ig}$ runs over $(-\infty, \infty)$. The lower horizontal thin line shows that the equation $-z_{ig} = \text{Li}_s(-z_F)$ has a single root for each $z_{ig}$ or $z_F$ value as well as for each of the considered $s$ values. On the contrary, the upper horizontal thin line illustrates a case where the equation $z_{ig} = \text{Li}_s(z_B)$ has no roots.

It is defined throughout the physical ranges of variables $T_F$, $V_F$ and $z_F$ and the ranges of the resulting variables $T_{ig}$, $V_{ig}$ and $\mu_{ig}$ coincide with their relevant physical ranges. The transformation is also reversible. [This property, trivial for the first two variables, holds true for variables $z_{ig}$ and $z_F$ owing to the reported properties of the relevant $\text{Li}_s(z)$ and it is also made evident by Figure 1.] Then, the substitution of (82) into (26) and the comparison of the result with equation (74) yield

$$\Omega_{ig,D}(V, T, \mu_{ig}(\mu_F, T)) = \frac{1}{g_F} \Omega_{F,D}(V, T, \mu_F),$$

that is condition (16) with $C_{AB} = 1/g_F$. A corollary of this result is the property that, whatever the positive integer $D$, the ideal Fermi gases and the ideal classical gases as well as the one dimensional hard rod gas are all thermodynamically equivalent among themselves, i.e. they form a class of thermodynamically equivalent systems. This property follows from the transitiveness property $(e)$ and the thermodynamical equivalence of the $D$-dimensional ideal classical gases proved in section 3.

It was already noted that the thermodynamic equivalence does not imply the equality of corresponding thermodynamic quantities as, for instance, the
entropies. In fact, the entropy of the Fermi gas is always positive \(^{[2]}\) while that of the ideal gas can be negative \(^{[13]}\). Since they are related as in equation \((53)\), it follows that \(\partial \mu_{ig}(\mu_F, T)/\partial T\) is negative within the \((\mu_{ig}, T)\) subdomain where \(S_{ig}(V, T, \mu_{ig})\) is negative.

One proves now that, for a given \(D\), the ideal Bose gas is not thermodynamically equivalent to the ideal gas, if the temperatures and the volumes of the two systems are assumed to be equal. To this aim, it is observed that, as \(z_B\) ranges over the physical range \([0, 1)\), function \(\mathrm{Li}_s(z_B)\) ranges over \([0, \zeta(s))\) [see equation \((80)\)]. Hence, at fixed \(T\), \(\Omega_{B,D}(V, T, \mu_B)/\left[\frac{g_B V k_B T}{\lambda^2}\right]\) ranges between \([0, \zeta(s))\) as \(\mu_B\) spans its physical range \((-\infty, 0)\). On the contrary, for the ideal gas, one finds that \(\Omega_{ig}(V, T, \mu_{ig})/\left[\frac{V k_B T}{\lambda^2}\right]\) ranges over \((-\infty, 0)\) as \(\mu_{ig}\) ranges over its physical range \((-\infty, \infty)\). The ranges of the two grand potentials are different and, therefore, the necessary condition, given by property \((a)\), for the thermodynamical equivalence of the two systems is not obeyed. Thus, the proof of the non equivalence is achieved. A consequence of this result is that, whatever \(D\), the ideal Fermi gas is not thermodynamically equivalent to the ideal Bose gas otherwise the last would be equivalent to the classical ideal gas in contradiction with what said just above. In other words, the ideal Bose gases belong to a thermodynamic equivalence class different from that of the Fermi ones. This conclusion deserves however some words of comment since it apparently contrasts the result obtained by Lee\(^{[14]}\). In fact, Lee proved that, if \(D = 2\), the one-to-one fugacity transformation \(z_F = z_F(z_B) \equiv z_B/(1 - z_B)\) relates the grand potentials of the Bose and Fermi gases (outside the Bose condensation region so as to avoid Pathria’s criticism\(^{[15]}\) and under the assumption that \(g_B = g_F\)) as follows

\[
\Omega_{B,2}(V, T, \mu_B) = \Omega_{F,2}(V, T, \mu_F) + \frac{k_B T V}{2} \lambda^2(T) \rho_B(z_B),
\]

where

\[
\rho_{B,2}(z_B) = \rho_{F,2}(z_F(z_B)) = \frac{g}{\lambda^2} \mathrm{Li}_1(z_B)
\]

are the particle number densities of the Bose and Fermi gases at the related fugacities. Since relation \((85)\) does not conform to \((16)\) for the presence of the further contribution \(k_B T V \lambda^2 \rho_B\) dependent on \(V\), \(T\) and \(\mu_B\), it is clear that Lee’s conclusion does not contrast with our non-equivalence conclusion.

6 Conclusion

The consideration of the reversible transformations between the state variables of different physical systems naturally leads to the definition of thermo-
dynamically equivalent systems. This paper considered the most restrictive definition of the thermodynamic equivalence which implies appropriate constraints on the codomains of the equivalent thermodynamic potentials as well as the similarity of the phase diagrams for the thermodynamic equivalence to occur. The most interesting feature of the definition is the possibility of dividing all the physical systems into classes of thermodynamically equivalence. Some examples of physical systems that are or are not thermodynamically equivalent were reported. One class of thermodynamic equivalent systems is formed by the ideal classical and quantum Fermi gases in any space dimensions and the one dimensional hard rod gas. Another class is formed by the systems where the particle interaction can be brought to coincide by a scaling of the distance as well as of the coupling constant. Since these systems show phase transitions, they are therefore endowed of similar phase diagrams. Finally, the ideal quantum Bose gases are not thermodynamically equivalent to the ideal Fermi ones. It is also stressed that the thermodynamic equivalence of two different physical systems does not ensure that all the thermodynamic quantities of one system are equal to the corresponding quantities of the other system. It does only ensure that the quantities are linearly related among themselves with coefficients that depend on suitable (partial) derivatives of the state variable transformation.
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